VOL. XLVI 1924

TRANSACTIONS of the American Electrochemical Society

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Forty-Sixth Meeting of the American Electrochemical Society
Detroit Mich. Oct. 2, 3 and 4. 1924.

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TRANSACTIONS

OF THE

American Electrochemical Society

VOLUME XLVI

FORTY-SIXTH GENERAL MEETING

DETROIT, MICHIGAN

OCTOBER 2, 3 AND 4, 1924

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VOLUME XLVI 1924

TRANSACTIONS

OF THE

American Electrochemical Society

PROCEEDINGS

CONDENSED MINUTES AND RECORD OF THE FORTY-SIXTH GENERAL MEETING OF THE SOCIETY, HELD AT THE HOTEL TULLER, DETROIT, MICHIGAN, OCTOBER 2, 3 AND 4, 1924.

The registration at this meeting was 113 members and 113 guests, or a total attendance of 226. Registration of members and guests began at 3.00 P. M., Wednesday, October 1st, in the ballroom of Hotel Tuller.

At 6.00 P. M. members and guests left the hotel for the St. Clair Country Club, where E. L. Crosby, Chairman of the Local Committee, had arranged for a most delightful "Get-Together" wild duck dinner.

PROCEEDINGS OF THURSDAY, OCTOBER 2, 1924

The first session of the Forty-sixth Meeting of the Society was held in the ballroom of Hotel Tuller. The session opened at 9.30 A. M., with President Parmelee in the Chair. After a few introductory remarks, Mr. Parmelee turned the session over to Dr. B. D. Saklatwalla, chairman of the symposium on "Corrosion." Six papers were presented at this session. The symposium was continued in the second session of the meeting, opening at 2.00 P. M. on Thursday, when five papers were presented, making a total of eleven papers on this important subject of "Corrosion." The

papers, which appear in full in this volume, were prepared by the following authors: F. N. Speller; Cecil H. Desch; Ulick R. Evans; J. Newton Friend, D. W. Hammond and G. W. Trobridge; W. H. Hatfield; F. N. Speller and F. G. Harmon; C. M. Kurtz and R. J. Zaumeyer; E. W. Greene and O. P. Watts; Wm. E. Erickson and L. A. Kirst; Colin G. Fink and L. C. Pan; H. S. Rawdon and A. I. Krynitsky.

At 12.30 a Round Table Discussion on "Electric Furnace Cast Iron," in charge of G. K. Elliott, was held at the Hotel Tuller. Discussion was opened by Dr. Richard Moldenke, who had recently returned from a trip to Europe. Dr. Moldenke described the Krupp desulfurizing process, as used at the Bielefeld plant in Germany. The first step in the process is the addition of ½ to 1 per cent soda ash, and after this has reacted, slacked lime is added to absorb the soda. The operation is carried out in a forehearth and a large slag chamber is in back of the furnace. The sulfur content of the cast iron used to run 0.22 per cent, but after introducing the Krupp process, the sulfur ran between 0.045 and 0.065 per cent for six months' operation.

There were 150 present at the Round Table Discussion, and it lasted for about five hours. Among the topics discussed was the disposal of the ever-increasing stock of cast iron borings. One operator reported using about 122 tons of borings a day in a 20-ton induction furnace. However, it was necessary to control the source of supply of borings, in order to insure absence of foreign material, such as brass and copper. Another operator found that the cost of melting down borings in the electric furnace was about three-fourths that of cupola iron. One of the furnace manufacturers emphasized the importance of the capacity of the plant as an item in arriving at the costs. With fuel-fired furnaces it is not unusual to operate a 500-ton plant, whereas when melting borings in an electric furnace, the individual heat averages about three tons. The electric furnace has been found serviceable in the manufacture of cast iron radiators and also for making cast iron piping. The acid-lined furnace is preferable to the basic lined.

A large party of members and guests left Hotel Tuller at 2.00 P. M. to visit the River Rouge plant of the Ford Motor Company.

A smoker in the Hotel Tuller ballroom and a theater party for the visiting ladies concluded the activities of the first day of the meeting.

PROCEEDINGS OF FRIDAY, OCTOBER 3, 1924

At 9.00 A. M. the technical sessions continued with a symposium on "Industrial Electric Heating," in charge of Prof. C. F. Hirshfeld. Papers by A. E. White, R. H. MacGillivray, Robert M. Keeney, F. S. Heath, and Harry Allen were presented and discussed. The meeting was then turned over to F. A. J. FitzGerald, and the subject of "Refractories for Electric Furnaces" was taken up. This symposium had been arranged by Dr. M. L. Hartmann, who, however, was prevented from presiding on account of illness. The papers presented were by the following authors: M. L. Hartmann and O. B. Westmont; C. E. Sims, H. Wilson and H. C. Fisher; and Frank T. Sisco. These papers, together with the discussion, are printed in full in this volume.

"Control Methods in Electrodeposition" was the subject under discussion at the Round Table Luncheon, held at 12.30 P. M. This Round Table was presided over by Prof. O. P. Watts and Dr. Wm. Blum. A number of the representatives of large plating plants reported that they had been using high school boys for carrying out the analytical control. It was pointed out that it is most important to control the raw materials, and avoid introducing into the bath impurities that might be contained in the raw materials. One of the engineers suggested that what was most needed in the electroplating shops today was an automatic indicator of the quality of the solution. At present it often requires several hours before the report of the analyst is received, and in the meantime considerable work may be spoiled or seriously delayed.

About one hundred members and guests visited the Cadillac and Hudson automobile plants, leaving Hotel Tuller at 2.00 P. M. Electric furnaces for heat-treating and for melting non-ferrous alloys were in operation at these plants and a number of interesting new processes were shown.

Technical sessions continued at 2.30 o'clock, and a number of

important papers were presented. The authors were: Fr. Foerster; Thomas P. Campbell; M. deK. Thompson; H. E. Haring; and Per K. Frölich. The papers appear in full in these Transactions.

At 8 P. M., before a large audience gathered in the Hotel Tuller ballroom, Alex Dow, President of the Detroit Edison Company, delivered an address on "Central Station Design and Superpower." Mr. Dow alluded to the changes in power-plant design since his address before the Society in 1917. Where heat-balance control for feed-water heating was common practice in 1917, turbine bleeding now is common practice, since it does not require the installation of expensive economizers. He also told some of the reasons why powdered fuel is used in the Trenton Channel power house. With investment costs per kilowatt of installed capacity in 1917 averaging $60, as against an average of $100 per kilowatt in 1924, Mr. Dow said that the increased expense to obtain higher thermal efficiency must be offset by the limits to which high investment charges can climb.

PROCEEDINGS OF SATURDAY, OCTOBER 4, 1924

The final session of the Detroit meeting opened at 9.00 A. M. Saturday. Papers by J. R. Cain; R. F. Mehl; Louis Kahlenberg and Herman H. Kahlenberg; H. C. P. Weber and R. H. Wynne; and A. E. R. Westman and R. B. Walker, were presented and discussed. These papers are printed in full in this volume.

At the end of the session, Dr. M. Sem, of Kristiania, Norway, gave a brief description of the recent developments in the Söderberg electrode.

In concluding the forty-sixth meeting, the following resolution was passed:

RESOLUTION OF THANKS

The American Electrochemical Society, in closing its forty-sixth meeting, wishes to extend a vote of thanks to the following:

The local committee, E. L. Crosby, chairman, for adequately providing for the comfort and entertainment of members and guests.

The ladies' committee, Mrs. Crosby, chairman, for their untiring efforts in lavishly entertaining the visiting ladies.

Mr. Alex Dow, for his unusually instructive and entertaining address on "Central Station Design and Superpower."

The St. Clair Country Club, for providing facilities for golf and dinner.

The Ford Motor Company, for supplying guides to show members through the River Rouge plant.

The Cadillac and Hudson Motor Companies, for taking members through their plants.

Hotel Tuller, for the use of meeting rooms and service provided to insure the comfort of guests during the meeting.

At 1.00 P. M. President Parmelee declared the meeting adjourned.

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A paper presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 3, 1924, President Parmelee in the Chair.

THE ELECTROLYSIS OF AMMONIACAL ZINC CARBONATE SOLUTIONS.[1]

By Thomas P. Campbell.[2]

Abstract.

The more important electrochemical properties of solutions of zinc in ammoniacal ammonium carbonate solvents are outlined, and the applications to hydrometallurgical practice are briefly considered.

Among the many schemes devised for the extraction of zinc from its ores there is a group in which the basic reaction is the formation of a complex ammonia salt of the metal. There are a number of these salts known.[3] Of the various solvents possible in this group, the ammoniacal carbonate solution has received the most attention,[4] although recently the use of hot, concentrated ammonium sulfate has been recommended.[5]

As a means of separating zinc from its ores or from other metals the ammoniacal carbonate solvent is very effective and possesses certain distinct advantages, chief among which is the fact that, comparatively speaking, only a few other metals form water-soluble ammono-carbonate salts. This makes the purification of the zinc solutions relatively easy and cheap. One of the main disadvantages connected with the use of any ammoniacal solvent is, of course, the extreme volatility of ammonia.

Of the common metals other than zinc which may be present

[1] Abstract of thesis presented to the faculty of the Colorado School of Mines in partial fulfilment of the requirements for the degree of Doctor of Science. Manuscript received June 7, 1924.

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[3] Mellor, Comprehensive Treatise on Inorganic and Theoretical Chemistry, vol II, p. 349, 1922.

[4] U. S. Pat. No. 585,355, Burghardt & Rigg, 1897; U. S. Pat. No. 654,804, Anthony Rigg, 1900; U. S. Pat. No. 1,204,843, Bretherton and Wilson, 1916.

[5] U. S. Pat. No. 1,445,366, E. P. Stevenson, 1923.

in an ore, Cu and Cd are the most readily soluble in this medium. Fe and Pb are so sparingly soluble that their presence is not to be feared, while As, Sb, Bi, Co, Ni, Mn, V, etc., are either only slightly soluble or are readily removed—especially in the presence of copper—by precipitation on zinc.

The electrodeposition of zinc from solutions of this type presents some unusual and significant aspects. The normal single potential of zinc is about — 0.76 volt,[6] yet zinc is deposited from ammoniacal carbonate solutions at a minimum potential of — 1.11 volts, in spite of the fact that the "hydrogen overvoltage" at zinc, at low current densities, is given as only — 0.72 volt.[7]

The explanation of this apparent abnormality lies in the extremely low H^+ ion concentration of ammoniacal solutions (less than 10^{-7} normal). Obviously, in such solutions the potential required to liberate hydrogen cathodically must be greater than that necessary in, say, normal $ZnSO_4$ solution. In short, as the H^+ ion concentration decreases, the hydrogen overvoltage increases; and thus it is possible to deposit zinc cathodically at potentials ranging from — 1.11 to — 1.15 volts.

GENERAL PROPERTIES AND REACTIONS.

The chemical constitution of the compound formed when zinc or zinc oxide is dissolved by an ammoniacal solution of ammonium carbonate is not given in the literature. The zinc-bearing solutions are comparatively heavy,—but not so much so as to interfere with settling,[8]—smell strongly of ammonia, and hydrolize on dilution, giving a precipitate of basic zinc carbonate. These solutions are decomposed by heat (steam) to yield a basic zinc carbonate and ammonia. The former loses water and carbon dioxide on calcination, forming a crystalline oxide.

From measurements of the solubility of zinc in solutions of constant ammonia and variable CO_2 content, it was found that: first, the ratio Zn/CO_2 is constant at 65.4/44; and, second, the ratio Zn/NH_3 approaches a value of 65.4/68. That is, when the total ammonia in the solution is combined one-half as hydroxide and one-half as carbonate, maximum solubility of zinc is

[6] Lewis & Randall, Thermodynamics, N. Y., 1923, p. 433.
[7] Knobel, Trans. Am. Electrochem. Soc., 43, 55 (1923).
[8] A solution containing 120 g. Zn per L. has a sp. gr. of about 1.18 at 25° C. The solvent solution from which this was prepared showed a sp. gr. of 1.063 at the same temperature.

obtained, and the resulting compound has the apparent structure, $ZnCO_3.4NH_3$.

Electrical transference experiments (Hittorf) showed that the NH_3 is associated with the zinc in the cation. That is, the correct representation of the structure would be $Zn(NH_3)_4CO_3$.

The transport number of the cation in a solution normal with respect to zinc at 25° C. was found to be 0.57.

The reaction between ZnO and the solvent may then be represented in the sense of the following equation:

$$(1)\quad ZnO + 2NH_4OH + (NH_4)_2CO_3 = Zn(NH_3)_4CO_3 + 3H_2O.$$

The zinc compound ionizes in solution thus,

$$(2)\qquad Zn(NH_3)_4CO_3 = Zn(NH_3)_4^{++} + CO_3^{--}.$$

For the passage of two equivalents of electricity through the solution we then have,

(3) At the cathode, $Zn(NH_3)_4^{++} + 2F = Zn + 4NH_3$,

(4) At the anode, $CO_3^{--} + H_2O - 2F = H_2CO_3 + O$,

(5) And in the body of the solution,

$$H_2CO_3 + 4NH_3 + 4H_2O = (NH_4)_2CO_3 + 2NH_4OH.$$

Thus the solvent is regenerated, and the net reaction on electrolysis may be written,

$$(6)\quad Zn(NH_3)_4CO_3 + 3H_2O = Zn + 2NH_4OH + (NH_4)_2CO_3 + O.$$

VOLTAGE MEASUREMENTS.

Thus we see that the zinc in such a solution exists in the form of a complex cation. Since the degree of dissociation of such an ion is extremely small, we would expect that the single potential of zinc against such a solution would be much more negative than that found in a solution normal in zinc ion, Zn^{++}.[9] Also, since these solutions are basic in reaction, we would predict that the discharge potential of hydrogen at a zinc cathode would be

[9] Foerster, Elektrochemie Wässeriger Lösungen, p. 182, 4th Ed., Barth, Leipzig, 1923.

much more negative than that found in, say, a normal solution of HCl.

The experimental verification of these considerations is shown in Fig. 1, 2 and 3. Fig. 1 and 3 show the variation of cathode potential *up to and just beyond* the decomposition point. Fig. 2 shows the change of anodic, cathodic and total cell polarization voltages with current density *above* the decomposition point. All single potentials were measured against the normal calomel element (0.283 volt at 25° C.), and are referred to the normal hydrogen electrode as arbitrary zero.

Fig. 4 shows the relation of total back e. m. f. to zinc concentration and current density. From Fig. 1 it will be noticed that the discharge potential of hydrogen (curve marked "solvent") is approximately — 1.18 volts, while that of zinc at 114 g. per L. is about — 1.12 volts.

In these experiments, and in all others involving change of zinc concentration, the dilutions were effected by withdrawing a known amount of solution of a given concentration and replacing it with the same volume of solvent solution. Thus the conditions obtaining in actual electrolysis, as given by the equations above, can be duplicated. The results are, then, a measure of the conditions which would prevail in an electrolytic cell at a corresponding stage of the electrolysis.

CONDUCTIVITY MEASUREMENTS.

Measurements of conductivity were carried out in the usual manner.[10] A vacuum tube oscillatory circuit was used as the source of high-frequency a. c. in the first experiments; later a Leeds & Northrup high-frequency generator was used. The results checked within the limits of experimental error, ± 0.3 per cent. A typical set of data is shown plotted in Fig. 6. The values of specific conductance were derived from the value for $N/50$ KCl, given by Kohlrausch and Holburn as 0.002737 mho per cm. cube at 25° C.

The total voltage of a cell in operation is made up of two main parts: the back e. m. f. of polarization, and the ohmic drop through the solution. Contact losses between the electrodes and

[10] Allmand, Applied Electrochemistry, N. Y., 1920, ch. VI.
Washburn, Principles of Physical Chemistry, ch. XVI, 1915.
Foerster, 4th Ed., Leipzig, 1923, ch. VI.

the bus-bars, and the ohmic losses in the connections and electrode materials should also be taken into account. For our present purposes, however, we may lump these in with the general ohmic drop without introducing any serious error. Thus,

$$V = E_{polariz.} + E_{ohmic} \tag{1}$$

Then for a cell in which the electrodes are 2.54 cm. (1 in.) apart, the ohmic resistance is given by

$$R = \frac{L}{kA} \text{ ohms per sq. dm.} \tag{2}$$

where L is in cm., A in sq. dm., and k in mho per cm. cube. If the current density is given in amperes per sq. dm.,

$$E_{ohmic} = \frac{C.\ D.}{39.4 \times k}\ . \tag{3}$$

Thus, using the data shown above, we can calculate the total voltage of a cell in operation at various concentrations and current densities. A set of such calculations is shown plotted in Fig. 7. The curve shown in broken lines is taken from data on zinc sulfate electrolysis given by Ralston.[11]

LARGE-SCALE LABORATORY EXPERIMENTS.

In order to verify these conclusions, and to gain a more definite idea of the conditions which would obtain in large-scale work, a series of experiments were performed using commercial reagents and a model-sized cell. The inside dimensions of the latter were: Length, 35.6 cm.; depth, 20.4 cm.; width, 15.2 cm. (14″ x 8″ x 6″). The cathodes were cut from 0.5 cm. aluminum sheet and were 15.2 x 10.2 cm. (6″ x 4″), with grooved wooden strips along the three immersed edges. The anodes were originally of mild steel; but these were later changed to high-chrome steel, 15.2 x 10.2 x 0.3 cm. (6″ x 4″ x ⅛″). This material proved very satisfactory for unattackable anodes, showing practically no corrosion after several weeks' use. The electrodes were placed in the cell in the usual alternate arrangement for 5 anodes and 4 cathodes, the spacing, anode to cathode, being 2.54 cm. (1 in.).

[11] Ralston, Hydrometallurgy and Electrodeposition of Zinc, N. Y., 1921, p. 85.

An aluminum cooling coil was used for temperature control; and the cell was provided with a water-sealed cover.

Due to the lightness of the cathodes, a great deal of trouble was experienced in obtaining good bus-bar contacts. However, the runs made showed very encouraging results. Some of these results, showing the effect of temperature rise, are plotted in Fig. 8.

APPLICATION TO PRACTICE.

In order to show the possibilities of commercial application, the following experiment is cited:

A mixture of oxides of the following composition was prepared:

	Per Cent
ZnO	55.80
PbO	8.46
Fe_2O_3	33.20
CuO	1.94
As_2O_3	0.07
Bi_2O_3	0.08
CdO	0.23
CoO	0.004
Sb_2O_3	0.004
NiO	0.08
MnO	0.15

The dry oxides were mixed thoroughly. An excess of leach liquor was added to a known weight of this mixture, and the whole was agitated in a closed pebble mill for six hours. The pulp was then settled and filtered, and the filtrate was run upward through a 732 x 7.6 cm. (24′ x 3″) cylindrical tower filled with zinc shot. The rate of flow was about 2 liters per hour. The precipitation of metals less electronegative than zinc took place vigorously, hydrogen being evolved at the zinc surfaces.

Due to the upsweep of the gases, and to the general upward movement of the solution, the slime metals were swept away from the zinc surfaces. Although used continuously for over 7 hours in this experiment alone, the tower showed no signs of clogging, nor was there any appreciable loss of precipitating power on the part of the zinc.[12]. Analysis of the spent oxides showed that 98.53 per cent of the zinc, and all of the Cu and Cd had been dissolved. Of the other oxides, PbO and Fe_2O_3 were not appreciably attacked; Cu, Cd, As, Sb, Bi, Co, Ni and Mn were found

[12] Hansen, Trans. Am. Electrochem. Soc., 44, 482 (1923).

in the metal slimes. The solution after final filtration was clear and light yellow in color, and contained 112.6 g. Zn per L. (The leach liquor contained 117.1 g. per L. NH_3 and 77.2 g. per L. CO_2.) Glue was added in an amount equivalent to 2.3 kg. (5 lb.) per ton zinc. This solution was then electrolyzed in the cell described above. The rate of circulation was 5 liters per hour. The temperature was allowed to rise to 33° C., and was then held at that point by means of the cooling coils. The results may be summarized as follows:

Average cell voltage	4.1
Average C. D.	3.84 amp. per sq. dm.
Ampere-hours	763
Zn sheet recovery	807 g.
Current efficiency	86.6 per cent

Analysis of the zinc sheets gave:

Fe	0.0183 per cent
Cd	0.0404 per cent
Pb	0.0124 per cent

The low-current efficiency and high voltage are both more or less directly traceable to poor electrode contacts. It is felt that an energy expenditure of not over 2900 kw.-hr. per ton zinc could be attained in practice—an expenditure which would compare favorably with that found in plants now in operation.

In fact, a process for the extraction and recovery of zinc from its ores, utilizing the electrodeposition from ammoniacal carbonate solutions, would compare well with sulfate practice. Assuming that the energy expenditures by the two processes are the same, the ammoniacal solutions would show a saving in purification, settling, filtration, etc., in that only one step is required to bring these solutions to the degree of purity necessary for successful electrodeposition of their zinc content. Further, the range of concentration over which the zinc may be economically recovered is considerably greater than would be possible in sulfate solutions. Thus it should be possible to reduce the zinc content from 120 to 10 g. per L. (approx. 1 lb. to 1.3 oz. per gal.) by electrolysis without undue lowering of the current efficiency. This cuts down the amount of solution required to maintain a given rate of production, and therefore represents a saving in equipment and operating charges.

For certain types of ores—especially those high in iron, lime and silicates—this process would seem very promising. Undue loss of ammonia by volatilization may be prevented by using covered or enclosed apparatus throughout. The use of water-sealed covers on the electrolytic tanks should prove satisfactory; and, in general, the use of enclosed equipment should not present any serious engineering difficulties. Iron or steel equipment—in the way of tanks, piping, pumps, etc.—can be used throughout, thus accomplishing a decided saving over lead or other acid-proof apparatus. The electrolytic tanks may be of wood or concrete; their number and arrangement would follow, in general, the tank-house layouts now in use. Due to the peculiar electrochemical properties of these ammoniacal solutions, the electrical connections would be somewhat different from those used in sulfate practice. The multiple, or Walker, system of electrode suspension can be used; but it would prove more economical to connect corresponding tanks in all cascades in parallel. Thus all the cells in a given cascade work at the same applied potential, the current dividing between the various cells according to the effective resistances. In this way, high-current densities are automatically produced at that stage of the electrolysis at which they are most efficacious and most easily obtained.

Fig. 9 shows the flow-sheet for a process of this type. The active agents in that part of the solvent carried off by the sludge can be recovered in the sludge dryer; *i. e.*, the NH_3 and CO_2 driven off by heat can be absorbed in suitable apparatus and returned to the system. Thus dilution due to the sludge washing is avoided, and no unnecessary step is added to the flow-sheet, since the sludge must be dried anyhow, and the process of drying thus fulfills a doubly useful function.

DISCUSSION.

Oliver C. Ralston[13] (*Communicated*[14]): The appearance of this paper is quite welcome as the possibilities of ammoniacal leaching of zinc ores are attractive. I shall take the liberty of asking a few questions.

[13] Berkeley, Calif.
[14] Communicated in advance of the meeting.

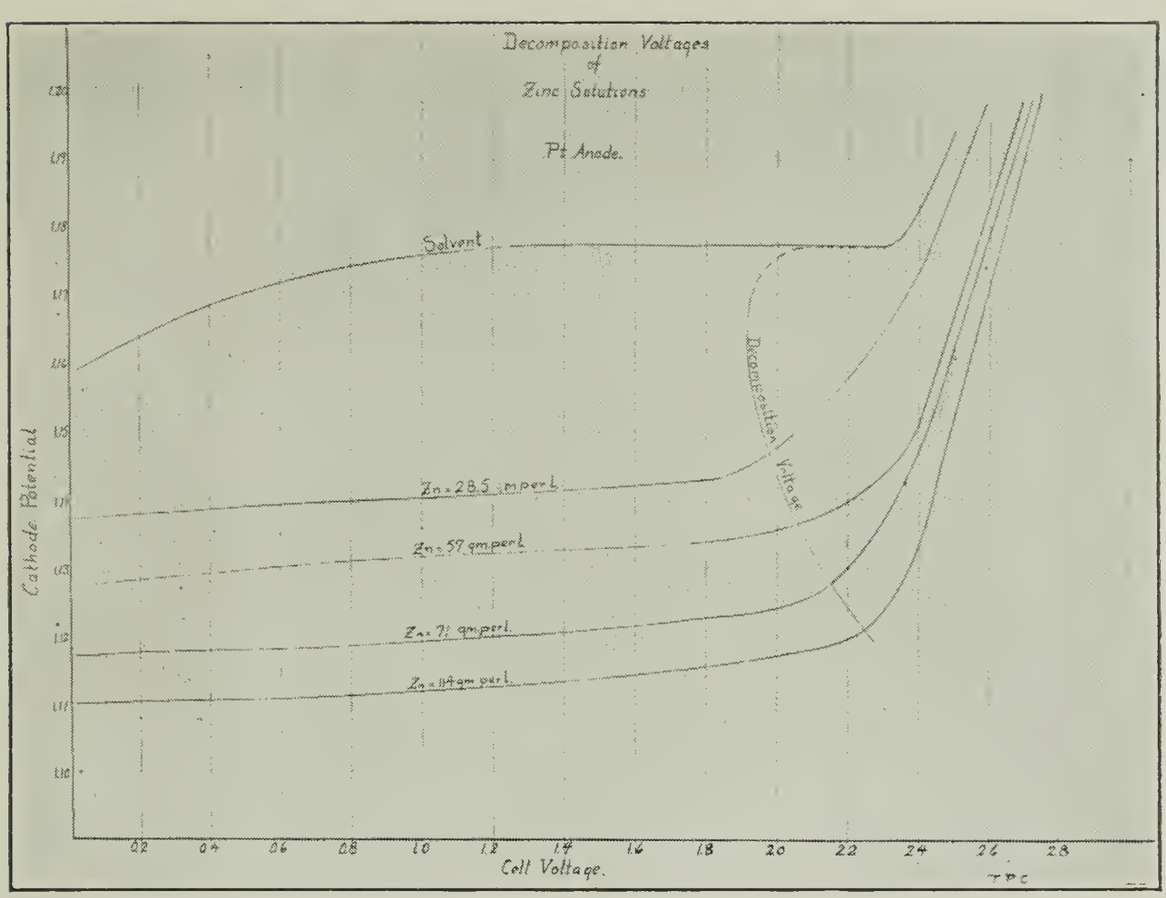

FIG. 1
Decomposition Voltages of Zinc Solutions (g./L.) Pt Anode.

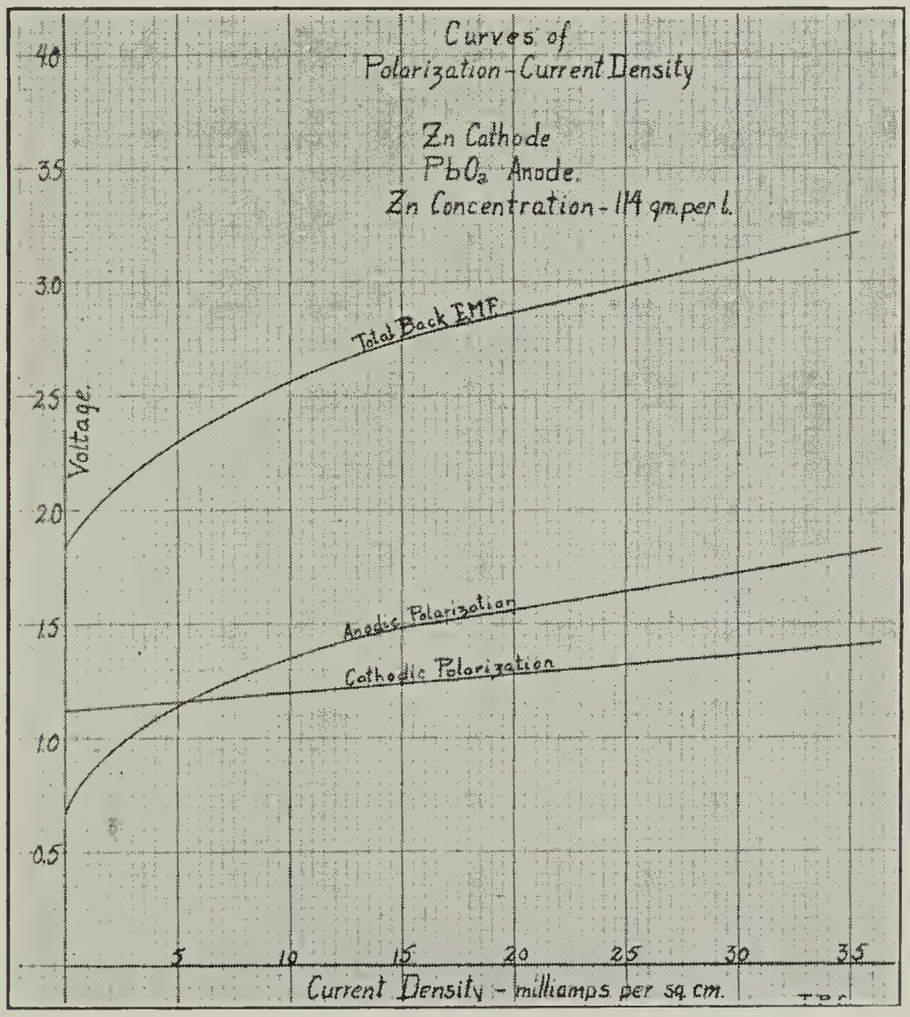

FIG. 2.
Polarization Voltage *vs.* Current Density.

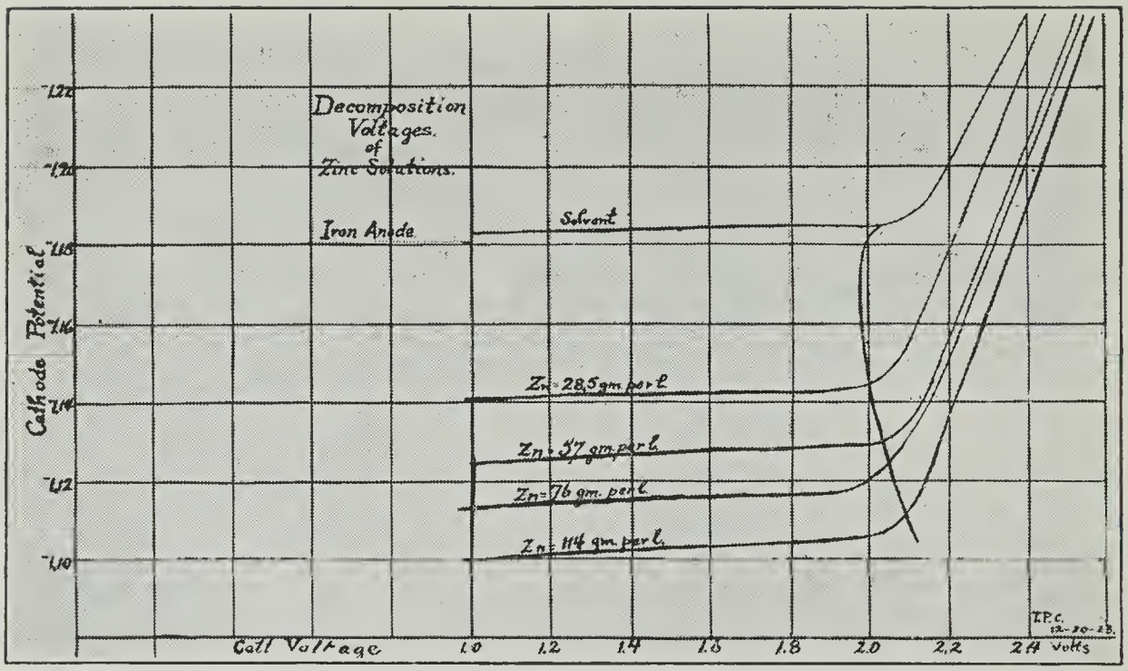

FIG. 3.
Decomposition Voltages of Zinc Solutions (g./L.) Iron Anode.

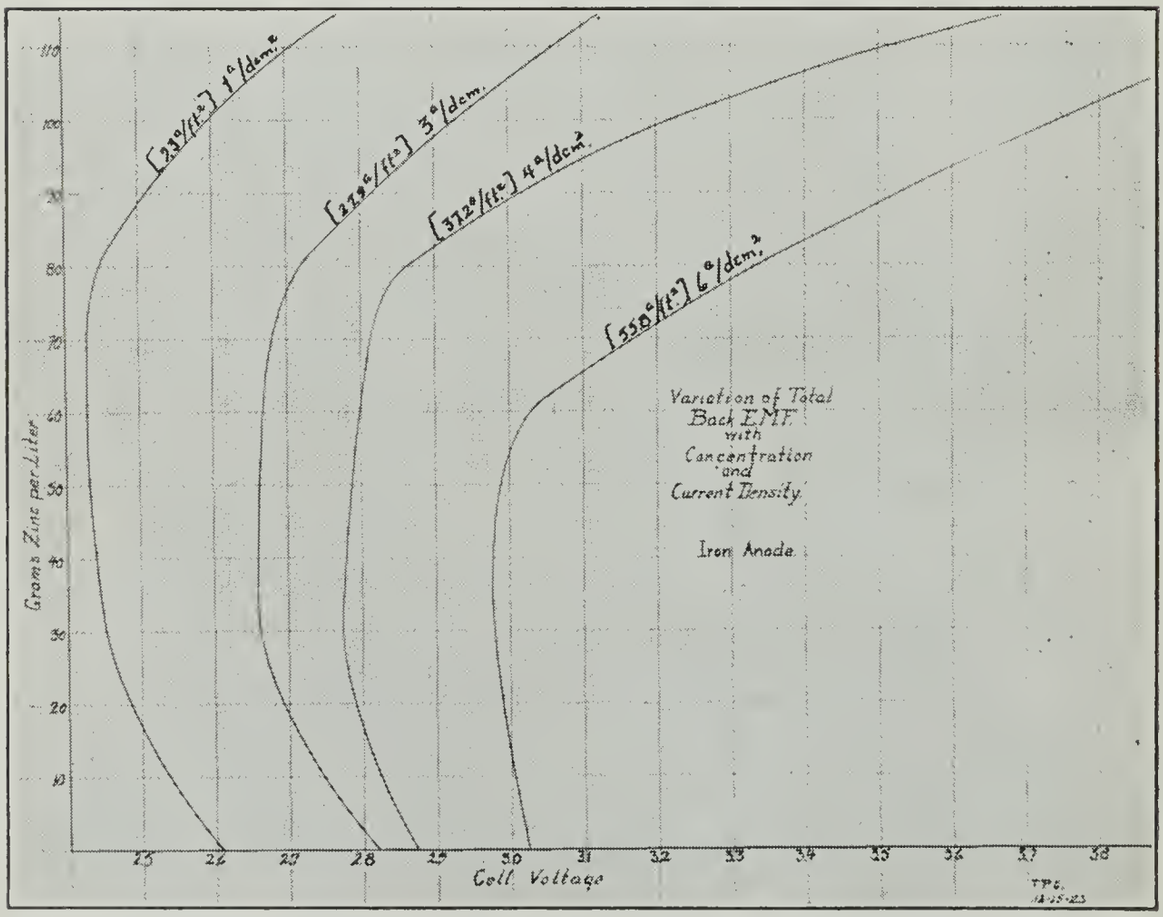

FIG. 4.
Variation of Total Back e. m. f. with Concentration of Zinc (g./L.) and Current Density.

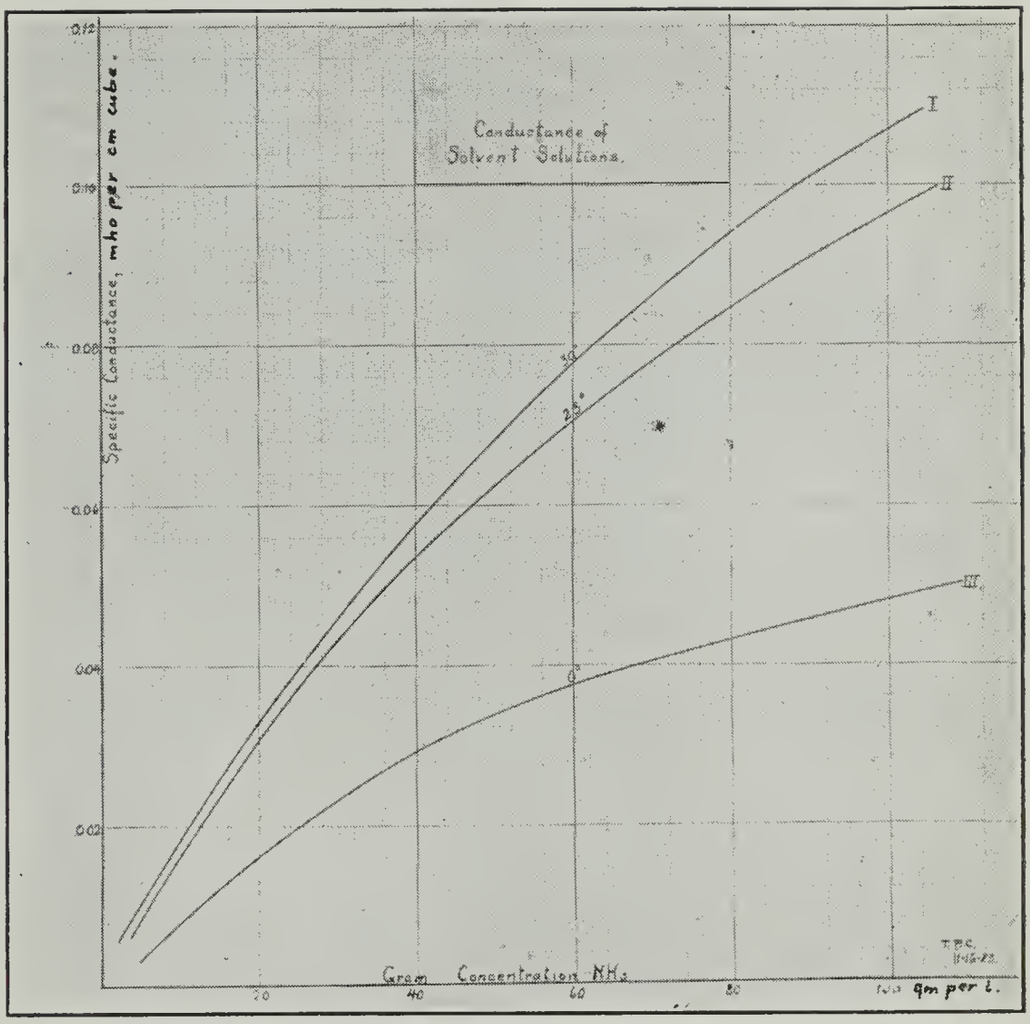

FIG. 5.
Specific Conductance (mho per cm. cube) at 0°, 25° and 30° C. of Solvent Solutions containing 2 g. to 110 g. NH_3 per L.

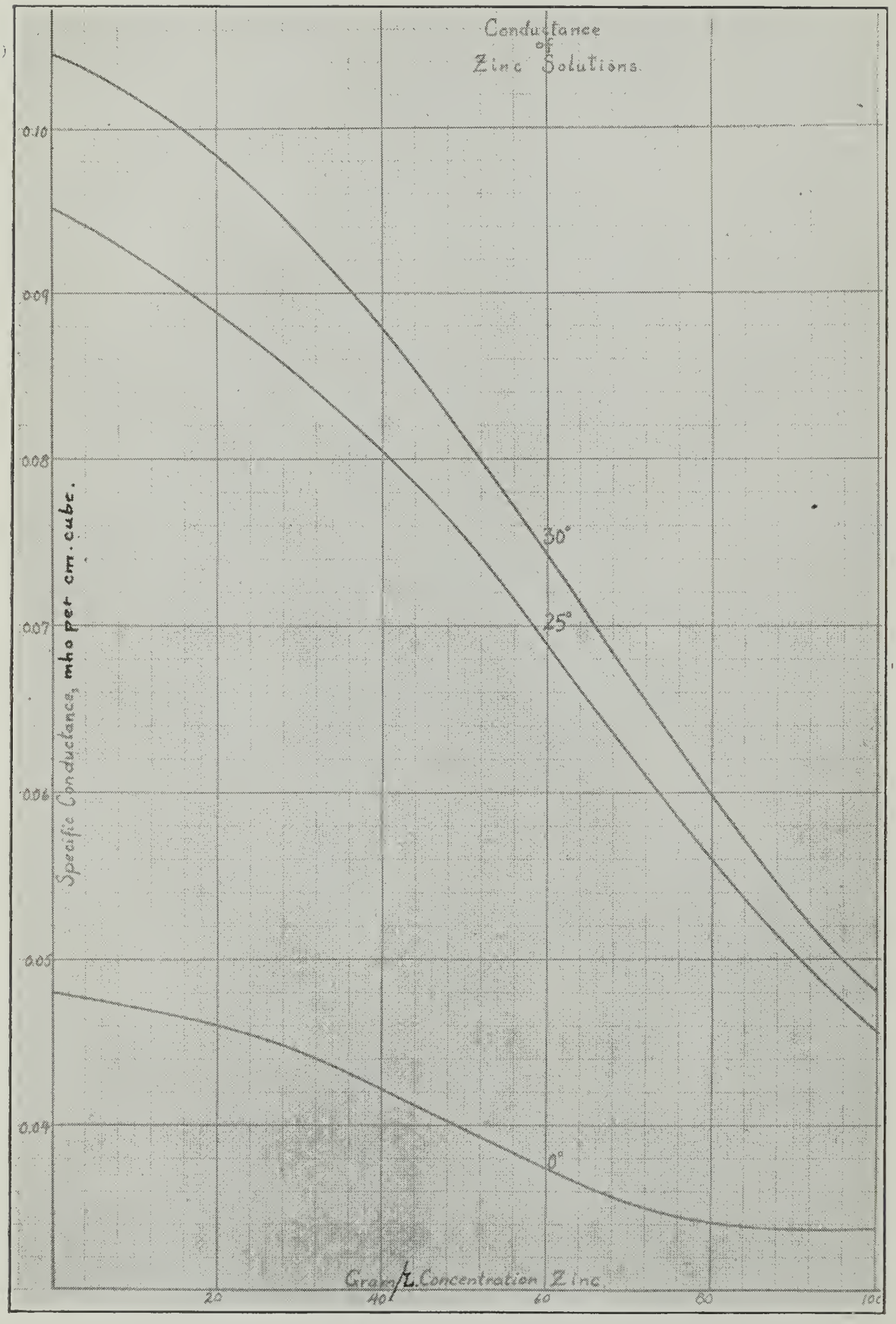

Fig. 6.
Specific Conductance of Zinc Solutions at 0°, 25° and 30° C.

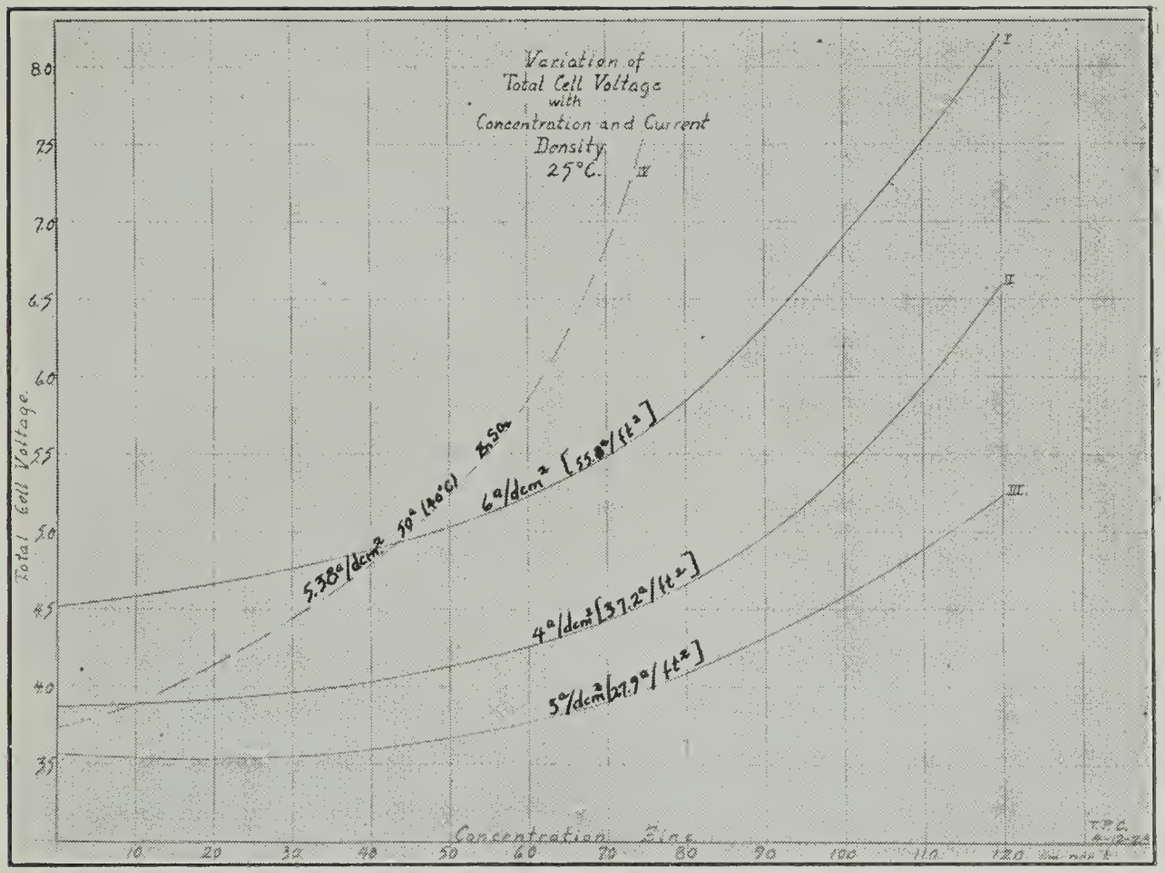

Fig. 7.
Variation of Total Cell Voltage with Zinc Concentration (g./L.) and Current Density, at 25° C.

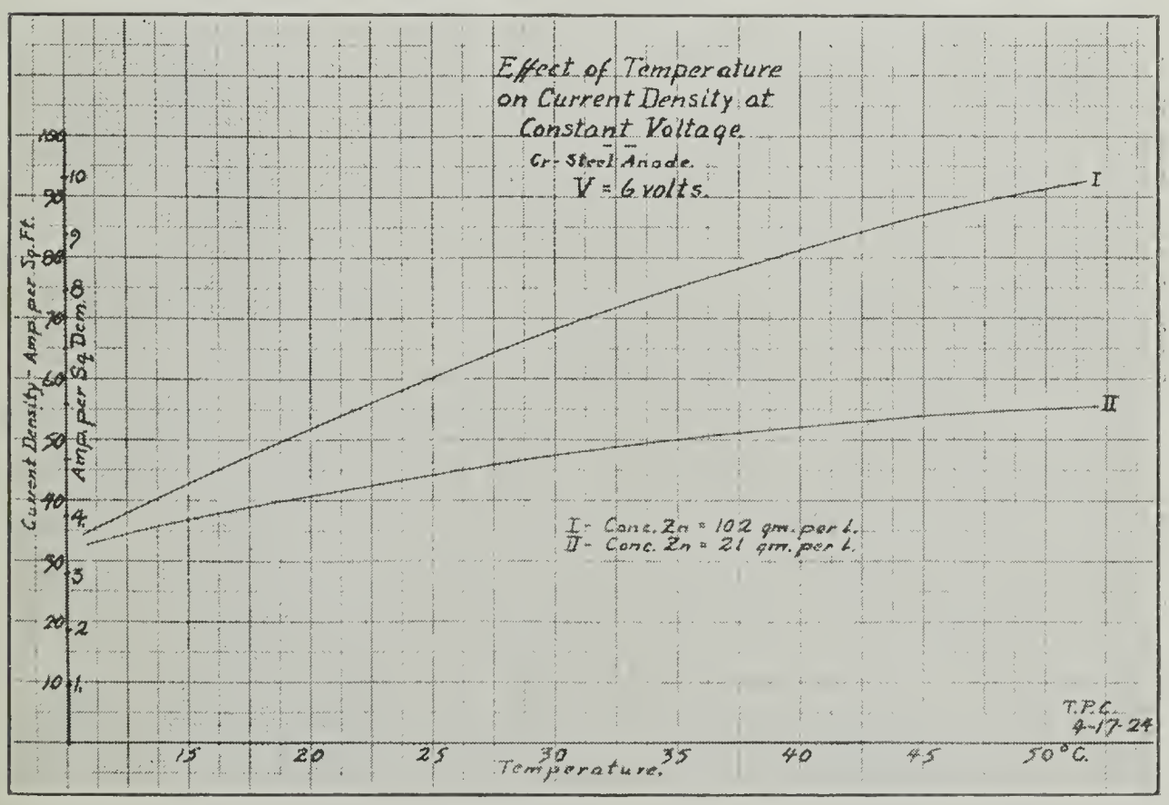

Fig. 8.
Effect of Temperature on Current Density at Constant Voltage (6 volts); Chrome-steel Anode.

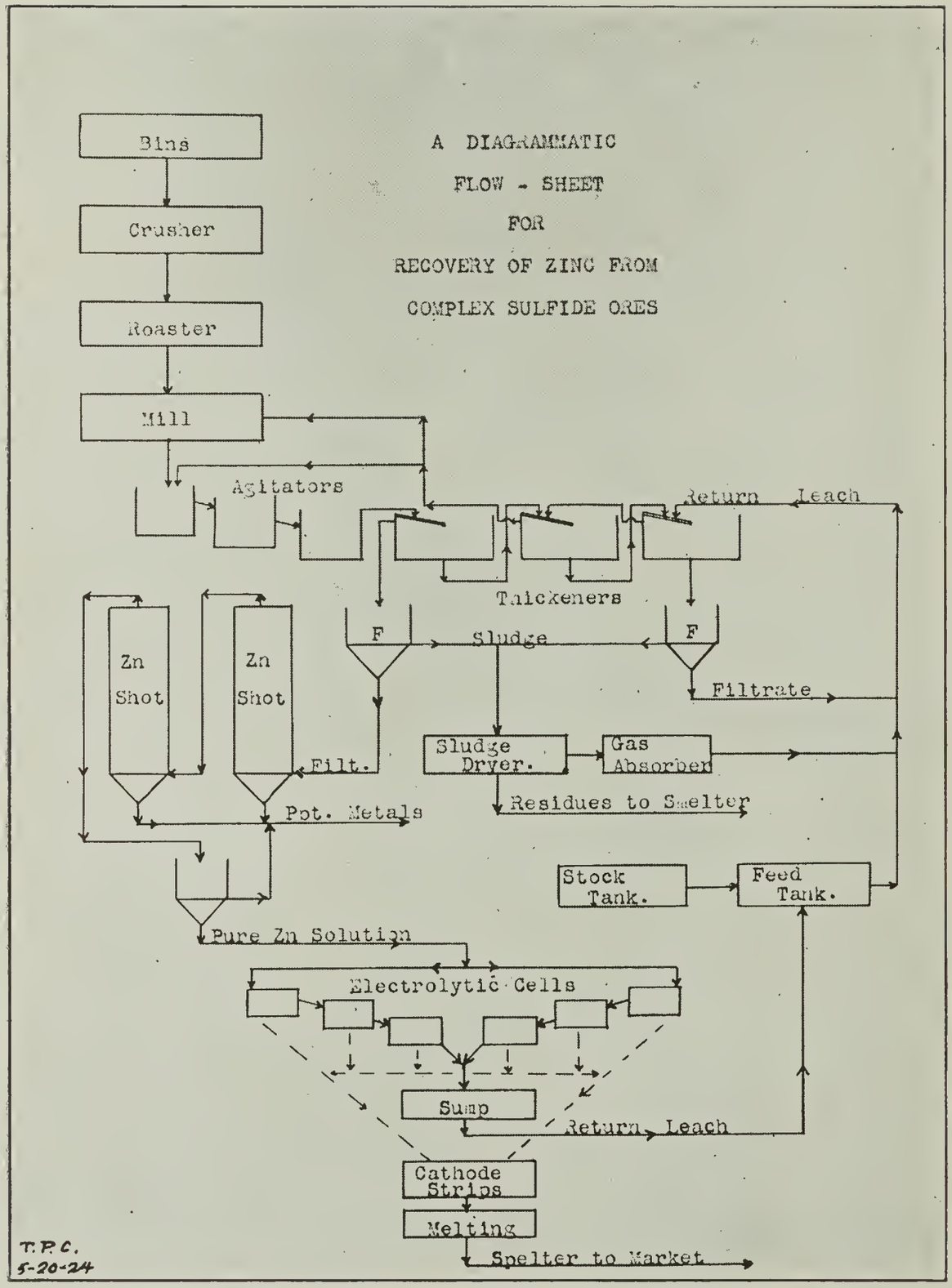

Fig. 9.
Flow Sheet for Recovery of Zinc from Complex Sulfide Ores.

1. Is there any difficulty in getting good cathodes? The use of glue in the solution suggests that the cathodes were not as smooth as might have been desired, and the suspicion that they tend to tree or to form spongy deposits. If treeing takes place the close spacing of electrodes (2.5 cm.) reported in the paper would not be permissible. In fact, a greater spacing in commercial work is almost necessary for other reasons, and with greater spacing comes the necessity of using higher voltage on the cell. The voltages reported seem a little high already, in comparison with sulfate practice, and this matter of voltage seems to work against the ammoniacal process.

2. Were any observations made of the ammonia concentrations before and after electrolysis? I would anticipate some loss due to decomposition of ammonia at the electrodes.

This whole matter of ammonia conservation is important, although crude gas-house ammonia, the cheapest form, is probably satisfactory. If roasted ore is used it is probable that satisfactory recoveries of ammonia, even from slimes, could be made; but the roasting introduces another undesirable feature, because any sulfates in the calcine will tend to "fix" ammonia as ammonium sulfate, so that the solutions will need frequent revivification. Just how this could be done is not exactly clear, but it is not an insuperable barrier to the development of a process.

It is also a matter of regret that this paper does not report results of leaching a calcine with the solutions, instead of using a synthetic ore. I anticipate low extractions of zinc by ammoniacal leaching solutions, as zinc ferrites and silicates would be difficult to treat by this method.

In general, while the results given in the paper are decidedly encouraging, there are many difficulties to be overcome before the process can be used in the treatment of complex ores. More likely, such products as brass-furnace flue-dusts, galvanizers' dross and similar by-products will prove better adapted to an ammoniacal leaching process.

T. P. Campbell: In reply to this discussion I wish to state at once that this paper makes no pretensions at covering all of the engineering and technical points which might be involved in such a process. The work which this paper covers was strictly of a

fundamental nature; the determination of those factors which are basic and requisite to the intelligent development of any electrochemical process.

As this fundamental or preliminary work is expanded and built upon, many of the points brought out by Mr. Ralston will be answered more fully than they can be now. At the present time these questions can be answered only in a general way.

1. Inherently these solutions should yield a better deposit of zinc than sulfate solutions, since, as pointed out, the zinc exists as a complex cation. As is well known, metals usually deposit more smoothly—that is, the crystal growth is less pronounced—when the concentration of metal ion, *per se,* is low. The use of an addition agent is made necessary by the presence of metals more noble than zinc in the solution. If these impurities could be completely eliminated, no glue would be required; and, as a matter of fact, the cathode deposits under such conditions are more satisfactory than those obtained from the same solution containing glue.

The tendency to sprouting or treeing is confined to the cathode edges. If the anodes are so proportioned and placed that the current lines from anode to cathode are divergent, thus avoiding "crowding" at the cathode edges, and if the edges are covered with wooden strips, the loss due to sprouting should not be excessive.

As noted in the paper, the high voltages reported were due in large part to poor contacts. Also, in comparing our data with those found in sulfate practice it should be remembered that in this case the temperature never exceeded 33° C., whereas in plant practice the temperature is seldom under 40° C. and may be as high as 100° C., as in Tainton's plant at Martinez, California. These ammoniacal solutions have a pronounced temperature coefficient of conductivity, especially at lower zinc concentrations. So that in practice good busbar contacts and higher solution temperatures (say 50° C.) will materially reduce the operating voltages.

2. I have been unable to detect any electrolytic decomposition of ammonia. Careful analysis of the gases escaping at the electrodes showed no traces of nitrogen. There is always a slight evolution of hydrogen at the cathode. The cell gases always

contain some ammonia, the more so as the temperature of the solution rises, so that in practice it would be necessary to scrub these gases for recovery of their ammonia content. Consultations with ammonia plant operators would indicate that an ammonia loss of 1 per cent should not be exceeded in practice.

The presence of sulfates in the calcines can be largely controlled by the conditions imposed on the roaster; some sulfating, however, is almost unavoidable when multiple-hearth roasters are operated at the rates demanded by economic factors. The resulting "fixation" of ammonia may be obviated by the addition of lime to the sludge, just before it goes to the dryers.

The synthetic calcine tests reported were supplemented by tests on roasted Leadville ores. These ores were roasted in a muffle furnace with hand rabbling. After a few experiments it was found that a slow, low temperature roast with thorough scavenging of the gaseous products led to satisfactory zinc extractions. There should be no more trouble, as regards ferrites, silicates, etc., in leaching zinc ores with these ammoniacal solutions than with seven to ten per cent sulfuric acid solutions. In fact, the leaching efficiency should be better in the case of ammoniacal solutions, since iron is not attacked, and silicates do not form gelatinous precipitates.

In addition to the zinc-bearing compounds mentioned by Mr. Ralston as the sources of zinc best adapted to ammoniacal leaching, I would mention the oxidized minerals of zinc, such as the carbonate and silicate, which are not readily amenable to concentration methods and which, on account of their lime gangue, are not suitable for acid leaching. These minerals, after calcination, yield satisfactory zinc extractions with ammoniacal solvents, as shown by tests on Leadville carbonates.

Colin G. Fink[15]: Personally, I think Mr. Campbell is to be congratulated. He started something. I appreciate the remarks made by Mr. Ralston. Of course, Mr. Ralston has been closely connected with the zinc industry, and he is naturally looking upon this paper from an industrial point of view. He does not appreciate, however, that every process has got to go through this preliminary laboratory stage. There is one other thing. Mr.

[15] Head, Division of Electrochemistry, Columbia Univ., New York City.

Campbell refers to the use of ferro-chrome anodes as insoluble anodes in an alkaline solution. Now, as a matter of fact, Prof. M. deK. Thompson[16] has been working for years with ferro-chrome anodes for making chromates, that is, using high chromium iron alloys as *soluble* anodes in making sodium and potassium chromate.

F. C. MATHERS[17]: How much glue was added?

COLIN G. FINK: If you use natural ores you will very likely introduce colloids into solution. You may not get the same effect with commercial ores that you do with synthetic ores. It is almost impossible in leaching a regular ore or concentrate with ammoniacal solution to avoid the formation of colloids, so that this addition agent question is a very important one.

W. BLUM[18]: It is difficult to see why glue should have any direct beneficial effect upon the structure of the cathode deposit. It certainly can not go directly to the cathode in an ammoniacal solution. It may, however, be acted on at the anode and thus give rise to secondary products, which have an effect.

T. P. CAMPBELL: In a solution which is very pure, that is, which was made up, we will say, of C. P. zinc oxide and C. P. chemicals all the way through, the effect of glue, or of any addition agent, is simply to increase the brittleness and density of the deposit. In the case of a solution carrying the impurities which you expect to find there, notably cadmium and copper, the effect of the glue is to minimize the effect of those impurities, and also to increase the density and brittleness of the deposit, but I have found by careful experiment that the presence of glue is actually beneficial in keeping down the tree growth.

F. C. MATHERS: Does this effect show instantly after the glue has been added, or must some time elapse before most of the effect is apparent?

T. P. CAMPBELL: I think I can answer that this way: I made one experiment in which a known amount of cadmium was present in the electrolyte, and a very poor deposit started. It was so bad, in fact, that it short-circuited the bath, due to the tree growth all

[16] This volume, page 51.
[17] Prof. of Chemistry, Univ. of Indiana, Bloomington, Ind.
[18] Chemist, Bureau of Standards, Washington, D. C.

over the surface of the cathode. While that liquor was being circulated through the tank, I added a solution of glue and water to the head liquors going into the tank, and changed the cathode starting strip at that time, and the resulting deposit on the fresh cathode strip was perfectly sound. A pre-determined amount of glue was added, and the effect seemed to be, therefore, almost instantaneous. The presence of glue does tend to raise the anodic polarization voltage somewhat, but I could not be sure of it because it was right on the line of experimental error, but it did seem to me that there was a slight increase there. I could not detect any increase in the cathode potential.

A paper presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 3, 1924, President Parmelee in the Chair.

THE ELECTROLYSIS OF HYPOCHLORITE SOLUTIONS.[1]

By F. Foerster.[2]

Abstract.

A very careful survey of the subject is presented, and it is shown that it is simply the potential at which the anions of the hypohalogenites are acted upon by the current, as compared with the discharge potentials of the corresponding halogen ions, which determines the course of the electrolysis of alkali halogenides; and that all the details and apparent peculiarities in the phenomena attending these electrolytic processes may be investigated and satisfactorily explained with the aid of these potentials.

I. Secondary Chlorate Formation.

Early investigations of the anode reactions in the electrolysis of alkali chloride solutions in the absence of a diaphragm showed that more or less hypochlorite is always formed in addition to chlorate. Careful study[3] of these reactions left no doubt that hypochlorite is the primary product of the anodic discharge of chloride ion, and that the hypochlorite in turn is converted into chlorate as it diffuses through the electrolyte. As electrolysis is continued, an equilibrium condition is approached in which the rate of formation of hypochlorite equals its rate of conversion to chlorate.

As for the mechanism of the hypochlorite-chlorate transformation, it was assumed at first to be the same as the purely chemical formation of chlorate, *viz.*, hypochlorous acid, formed anodically

[1] Manuscript received June 21, 1923. Translated from the original German by Dr. W. G. Horsch.

[2] Inorganic Chemical Lab. of the Technische Hochschule, Dresden, Saxony.

[3] F. Oettel, Z. Elektrochem., I, 354 (1894); F. Foerster and E. Müller, Z. Elektrochem., 6, 11 (1899).

by the discharge of hypochlorite ions, oxidizes undischarged hypochlorite ions.

$$2ClO^- + 2 \oplus \rightarrow 2ClO \qquad (1)$$

$$2ClO + H_2O \rightarrow 2HClO + O \qquad (2)$$

$$2HClO + ClO^- \rightarrow ClO^-_3 + 2Cl^- \qquad (3)$$

$$2H^+ + 2ClO^- \leftrightarrows 2HClO \qquad (4)$$

The formation of chlorate thus would occur secondarily as the result of purely chemical action; hence the process is termed *secondary chlorate formation.* On investigation, however, the velocity of reaction (3) was found to be by no means adequate to convert into chlorate the hypochlorite furnished by the current in the small layer of solution close to the anode where a somewhat larger concentration of free hypochlorous acid and an adequate concentration of its salt may be assumed. In this connection, it is to be observed that the constant, simple relationship between the quantities of active and of molecular oxygen formed under equilibrium conditions could be scarcely interpreted on this basis.

II. ANODIC CHLORATE FORMATION.

It follows, therefore, that the conversion of hypochlorite into chlorate is the direct result of the current, in other words, it is strictly electrochemical in nature. Determination of the decomposition potential of a pure, that is, chloride-free, 1.0 molal NaClO solution[4] showed that ClO^- in a chloride solution ought to take part in the anode reaction. This potential is about 0.3 volt lower than that of a normal NaCl solution. In other words, ClO^- is discharged, or oxidized anodically, at an anode potential about 0.3 volt less than is Cl^-. If, then, a chloride solution is electrolyzed, and the free chlorine which is liberated at the anode reacts with the alkali hydroxide simultaneously produced at the cathode, forming hypochlorous acid and hypochlorite,

$$Cl_2 + OH^- \leftrightarrows HClO + Cl^- \qquad (5)$$

$$HClO + OH^- \leftrightarrows ClO^- + H_2O \qquad (6)$$

[4] F. Foerster and E. Müller, Z. Elektrochem., 8, 634 (1902).

then the ClO^- must take part in the anodic reaction as soon as it has attained even a slight concentration at the anode.

This concentration at the anode evidently is consistent with an appreciable hypochlorite concentration in the electrolyte, since, as the result of anodic oxygen evolution on one hand, and of the presence of free chlorine on the other, ClO^- must be formed according to equation (5), but diffusing away in the form of the very weakly ionized, free hypochlorous acid. In harmony with this is the fact that at the beginning of the electrolysis of a neutral alkali chloride solution hypochlorite is formed at a very high current efficiency, especially when a platinized anode is used, which is one of the simplest cases; this means that the amount of oxygen evolved anodically is very slight. Only when a definite concentration of hypochlorite has been reached, does the current efficiency of oxygen evolution rise rapidly, reaching 33.3 per cent, the hypochlorite concentration then becoming constant, and chlorate, hitherto formed to only a slight degree, becoming the principal product of the electrolysis.

The next and most important problem in the development of the theory of alkali chloride electrolysis was the investigation of the manner in which ClO^- is acted upon by the current during the formation of ClO_3^- and free oxygen. This problem could be solved only provided the anodic changes involving ClO^- were followed most carefully and isolated from other anode reactions, and the reactions carried out in a solution initially as free as possible of Cl^-. When chlorine acts on alkali, Cl^- as well as ClO^- is formed. Hence, for the preparation of the electrolyte, it was necessary to start with a solution of pure hypochlorous acid. This acid is prepared readily in a thoroughly stable form at a concentration of 1 to 1.25 mols HClO per liter; the familiar method of distilling the solution produced by the action of chlorine on mercuric oxide suspended in water is used. The free chlorine developed during distillation is removed from the distillate by means of a current of air.

Such a solution possesses low electrical conductivity. Hence, in order to study the electrolysis, an indifferent electrolyte must be added. Phosphoric acid was found to be satisfactory for this purpose. In order to keep anode and cathode reactions separate, the electrolyte was introduced into a clay cylinder which was, in

turn, set into a second larger clay cylinder filled with dilute phosphoric acid. The second cylinder was surrounded by the catholyte, which likewise was a phosphoric acid solution; the cell was a glass beaker and the cathode a platinum foil of cylindrical shape. A similar smaller platinum cylinder served as anode. Under these conditions, chloric acid is formed anodically in the hypochlorous acid solution, and chlorine and oxygen are evolved. The quantities of these products, as well as the amount of undecomposed hypochlorous acid, were carefully determined analytically, and compared with the quantity of electricity put through the cell as measured by a copper coulometer. Experiments of this sort had been carried out previously by the writer,[5] at whose suggestion they were repeated, extended and carried out with great care by O. Jensen. The results thus obtained are presented in Table I. In order to facilitate comparison, the quantities of all the molecular species involved in the reactions, including free chlorine, are expressed in terms of equivalent oxygen.

According to Table I, if chlorine is liberated in addition to chlorate and free oxygen when a solution of hypochlorous acid is electrolyzed, it can occur only through the breaking up of ClO^- (formed as an intermediate step) into ClO_3^- and Cl^-, the latter being discharged anodically to form Cl_2. On the other hand, by regrouping the results as in Table II, the data show that the sum of the anodic oxygen and the oxygen equivalent of the anodically liberated free chlorine corresponds, within the experimental error, to the electric current consumed. This statement holds for various current densities and also regardless of whether the anode is smooth or platinized.

From this it follows that no anodically liberated oxygen can have been consumed in an oxidation process such as chlorate formation. Finally it will be noted that the ratio of free chlorine-oxygen to chlorate oxygen is always very nearly 1 : 3. Since, due to the presence of the phosphoric acid in the electrolyte, the anode potential is maintained high enough to insure the immediate and practically complete discharge of Cl^- as it is formed, it follows that the ratio of Cl^- to ClO_3^- generated electrolytically is 2:3. It is conceivable, therefore, that in the electrolysis of a solution of

[5] Z. Elektrochem., 8, 665 (1902).

hypochlorous acid the mechanism of the anode process is represented by the following equations:

$$6ClO^- + 6 \oplus \rightarrow 6ClO \qquad (1)$$

$$6ClO + 3H_2O \rightarrow 2ClO_3^- + 4Cl^- + 6H^+ + 3O \qquad (7)$$

$$4Cl^- + 4 \oplus \rightarrow 2Cl_2 \qquad (8)$$

that is, instead of the discharged ClO reacting again with water to form hypochlorous acid as in equation (2), it is decomposed by water to form chloric and hydrochloric acids. According to the experiments recorded in Table I (compare also Table II), the quantity of oxygen evolved is greater than corresponds to equation (7). This is not surprising since it is evident that, in view of the slight concentration of ClO^- which can exist in the presence of excess phosphoric acid, the OH^- of the water must also take part in the anode process. Hence for the sake of completeness the above reactions must be supplemented by the following:

$$2OH^- + 2 \oplus \rightarrow O + H_2O \qquad (9)$$

The electrolytic formation of chlorate according to equations (1) and (7) has been designated as *anodic chlorate formation* by Erich Müller and the writer.

The anodic reactions in a concentrated alkali chloride solution take place as follows: At first practically nothing except chlorine is discharged (equation 8). This reaction requires a potential of about 1.34 volts to take place reversibly at a platinized anode. Hydroxide ion, which is the only other anion present initially besides Cl^-, is dischargeable reversibly at 1.27 volt. However, the H^+ thereby set free at the anode would quickly increase to 20, 30 or more times its original very low concentration, thus rendering the reversible discharge of OH^- more difficult than that of Cl^-, if this discharge actually could take place reversibly. As a matter of fact, even a slight charging of the platinized anode by oxygen very soon checks the discharge of OH^- (reaction 9) to such an extent that as long as there is sufficient Cl^- at the anode for the current to act upon, the OH^- discharge may be practically neglected in comparison with the discharge of Cl^- at a platinized anode. But if ClO^- is formed by the interaction of the free

chlorine of the anode and the OH^- produced at the cathode (anions which at the same concentration are more readily acted upon by the current than Cl^-, and which also maintain a low H^+ concentration at the anode) then it is these ions which take part in the anode process according to equations (1) and (7) to a greater and greater extent, compared with that of Cl^-, as their concentration increases. This action is comparatively slight at first, but as their discharge potential, due to increased concentration, approaches that of Cl^-, presently their rate of discharge to form chlorate will equal their rate of formation in accordance with equations (5) and (6). This stationary condition may be represented by the following equations:

$$12Cl^- + 12 \oplus \rightarrow 6Cl_2 \qquad (8)$$

$$6Cl_2 + 12OH^- \rightarrow 6ClO^- + 6Cl^- + H_2O \qquad (5)+(6)$$

$$6ClO^- + 6 \oplus \rightarrow 6ClO \qquad (1)$$

$$6ClO + 3H_2O \rightarrow 2ClO_3^- + 4Cl^- + 6H^+ + 3O \qquad (7)$$

Reactions (8) and (5) + (6) give rise to active oxygen in the form of dissolved hypochlorite, whereas reactions (1) and (7) convert this active oxygen into another form, namely, chlorate-oxygen, and as such they are lost for the production of further active oxygen, liberating free oxygen gas. As soon as stationary conditions have been attained, the ratio of gaseous oxygen liberated to active oxygen formed will have become constant at 1 : 2, as shown by equation (7), and the current yield of active oxygen will be two-thirds of the theoretical. These phenomena recur constantly in the electrolysis of concentrated alkali chloride solutions; their complete agreement with the conclusions drawn from the experiments on the electrolysis of hypochlorous acids puts them on a sound basis.

In alkali chloride electrolysis, the attainment of the stationary conditions just described is dependent upon the following:

1. The ClO^- must take part in no other reaction except chlorate formation.

2. No other anode reaction must take place besides that of ClO^- and the discharge of Cl^-.

The first requirement is not fulfilled if the hydrogen liberated at the cathode reduces the ClO^- to Cl^- at that point. This reduction takes place readily, but may be prevented if a thin chromic oxide diaphragm is allowed to build up on the cathode through the addition of a small amount of chromate. The discovery of this phenomenon by Erich Müller[6] has made possible the exact investigation of the anode reactions in alkali chloride electrolysis. Indeed, the conditions stated above as requisite stationary conditions are valid only for solutions to which 0.2 per cent $KrCrO_4$ has been added in order to exclude cathodic reduction.

Another reaction which ClO^- may undergo is the purely chemical, secondary chlorate formation which may take place in the electrolyte according to equations (3) and (4). It presupposes collision between ClO^- and free HOCl, and its rate of reaction is given by the following equation:

$$\frac{dc_{ClO^-}}{dt} = KC_{ClO^-}(C_{HClO})^2$$

where the differential coefficient represents the diminution in hypochlorite concentration in unit time.[7] The value of the constant K is comparatively small. As long as ClO^- and HClO appear in somewhat greater concentration only in the immediate vicinity of the anode, that is, in a very small solution volume, the velocity of the reaction does not become appreciable. If, however, by acidifying the electrolyte, collisions between ClO^- and HClO are caused to occur throughout the whole solution, secondary chlorate formation may attain such a reaction velocity, especially if the temperature is raised, as to keep pace with direct electrolytic hypochlorite formation.

Under these circumstances the stationary state, as the net result of anodic and secondary chlorate formation, consists in the conversion of hypochlorite to chlorate as rapidly as it is produced by the current. Since, however, the latter takes place without the formation of oxygen, the current yield of chlorate will be higher the more the secondary formation of chlorate preponderates. Experiments have shown that the current efficiency of chlorate formation may be raised in this way to 85-90 per cent;

[6] E. Müller, Z. Elektrochem., 5, 469 (1899).
[7] Jour. f. prakt. Chem., 63, 141 (1901).

whereas in neutral solution it does not exceed 66.6 per cent. In commercial operation the electrolytic production of chlorate should be (and actually is) carried out in a hot, concentrated chloride solution, to which a little bichromate and hydrochloric acid have been added.

The second requirement, as stated above, for proper operation of alkali chloride electrolysis is not fulfilled if, in addition to Cl^- and ClO^-, OH^- takes part in the anode reaction, that is, if reaction (9) becomes appreciable. As was shown above, reaction (9) is really to be expected in a neutral, concentrated, chloride solution, but does not take place owing to certain special circumstances. However, it is apparent from the discussion referred to that this reaction (9) may become appreciable either when the ratio of the concentrations of Cl^- to OH^- becomes materially lower than that which prevails in a neutral, concentrated chloride solution, or when a change in the anode material reduces or eliminates the resistance of the reactions that oppose oxygen formation or, in other words, lowers the anode potential necessary for O_2 evolution from a given OH^- concentration. This reduction of the anode potential occurs, for example, upon coating a platinum electrode with cobaltic oxide or upon substituting a magnetite electrode.

With platinum as anode material, the ratio of Cl^- to OH^- will be the determining factor for OH^- discharge. Accordingly, if the chloride concentration in a neutral solution falls materially below that corresponding to saturation, the current efficiency in chloride electrolysis will fall below 66.6 per cent, especially if through a rise in electrolyte temperature the OH^- concentration of the water is increased and the oxygen gas polarization is reduced.

A similar effect might be expected if the OH^- concentration were raised, *e. g.*, by employing an alkaline chloride solution. As long as the addition of caustic is slight, this effect does not occur, due to the fact that the anodically liberated chlorine keeps the OH^- concentration right at the anode (that is, in the thin surface layer of solution which is effective in determining the course of discharge processes) far lower than in the rest of the electrolyte. However, this causes the concentration of ClO^-, which prevails right at the anode surface, to be increased in comparison with

that of the rest of the electrolyte. As the initial alkalinity is increased, the hypochlorite concentration at the stationary state of the electrolyte, as a whole, continually drops and stationary concentrations are attained more rapidly, until, ultimately, the stationary state sets in almost immediately after electrolysis is started, the hypochlorite concentration being exceedingly slight; the current therefore produces chlorate almost exclusively right from the start, and at a current efficiency not exceeding 66.6 per cent.

This phenomenon was first observed by Oettel[8] and experiments made by Nielsen have shown that it occurs with smooth platinum anodes in $3N$ NaCl solution when the alkali is about $0.3N$ at 18° C. or only $0.12N$ at 75° C. If the alkalinity of the electrolyte is further increased, the discharge of OH^-, in addition to that of ClO^-, begins to take place in an appreciable and increasing degree; the anodic evolution of oxygen considerably exceeds 33.3 per cent efficiency, while the current yield of chlorate is correspondingly repressed. The fact that Cl^- continues to be discharged in spite of the preponderance of the more easily discharged OH^-, is due to the strong self-polarization characteristic of oxygen at platinum anodes.

III. PRIMARY CHLORATE FORMATION.

If, with increased alkalinity, the concentration of the ClO^- right at the anode is no longer of the small order of magnitude of that of the HClO, but appreciably exceeds the latter, the question arises as to whether the conversion of ClO^- into ClO_3^- still takes place only by anodic chlorate formation. In this connection, it should be borne in mind that a slight current is produced in 1/1 molal alkali hydroxide solution at an anode potential as low as 0.9 to 1.0 volt, at least at a freshly platinized anode, and that even in this case, due to the depolarizing action of OH^- on the discharge of Cl^-, hypochlorite appears at a low concentration[9] and at potentials such as may actually occur in the electrolysis of 1-molal hypochlorite solution at a low current density. If a considerably more dilute hypochlorite solution is employed with a sufficiently high OH^- concentration, oxygen may be liberated through discharge of OH^- even while undischarged ClO^- is in contact with

[8] F. Oettel, Z. Elektrochem., 1, 474 (1894).
[9] F. Foerster and E. Müller, Z. Elektrochem., 9, 201 (1903).

TABLE I.—*Electrolysis of HOCl in Presence of Phosphoric Acid.*

Fifty cc. of electrolyte with 4 grams H_3PO_4. Anode 50 sq. cm. Room temperature.

Exp. No.	Anode	Amp.	Before the electrolysis there were in the electrolyte		Oxygen corresponding to the amount of current consumed g.	Total available oxygen g.	After the electrolysis there were in the electrolyte		During the electrolysis there have escaped		Total recovered oxygen g.	Loss of Oxygen Per Cent
			Hypochlorite oxygen g.	Chlorate oxygen g.			Hypochlorite oxygen g.	Chlorate oxygen g.	Oxygen corresponding to the free chlorine g.	Oxygen gas g.		
1	platinized	0.25	0.1739	0.0149	0.1501	0.3389	0.0575	0.1292	0.0397	0.1077	0.3341	1.4
2	platinized	0.50	0.1940	0.0172	0.1494	0.3606	0.0744	0.1360	0.0367	0.1097	0.3568	1.2
3	platinized	0.50	0.1339	0.0128	0.1506	0.2973	0.0361	0.1074	0.0316	0.1144	0.2895	2.6
4	platinized	1.0	0.2027	0.0224	0.1540	0.3791	0.0909	0.1254	0.0399	0.1162	0.3724	1.8
5	smooth	0.50	0.2275	0.0364	0.1522	0.4161	0.1194	0.1415	0.0411	0.1095	0.4115	1.0
6	smooth	0.50	0.0992	0.0066	0.0847	0.1905	0.0166	0.0824	0.0246	0.0588	0.1824	4.2

TABLE III.—*Electrolysis of NaOCl in Presence of NaOH.*

Fifty cc. of electrolyte. Anode, 50 sq. cm. of smooth platinum. Room temperature.

Exp. No.	Current in Amp.	Alkalinity before the electrolysis	Before the electrolysis there were present in the electrolyte			Oxygen corresponding to the amount of current consumed, g.	Total available oxygen, g.	Alkalinity after the electrolysis	After the electrolysis there were present in the electrolyte			Oxygen gas escaping during the electrolysis, g.	Total recovered oxygen, g.	Loss of oxygen, per cent
			Hypochlorite oxygen, g.	Chlorate oxygen, g.	Chloride, expressed in equivalent oxygen, g.				Hypochlorite oxygen, g.	Chlorate oxygen, g.	Chloride, expressed in equivalent oxygen, g.			
7	1.0	0.32-*N*	0.3431	0.0415	0.000	0.0876	0.4722	0.14-*N*	0.2894	0.1236	0.0119	0.0465	0.4714	0.2
8	1.0	0.50-*N*	0.5208	0.0270	0.0111	0.1003	0.6592	0.29-*N*	0.4549	0.1276	0.0253	0.0531	0.6609	0.2
9	1.0	1.05-*N*	0.4345	0.0173	0.0092	0.0769	0.5329	0.90-*N*	0.3927	0.0822	0.0188	0.0418	0.5355	0.5
10	2.0	1.09-*N*	0.4865	0.0219	0.0090	0.0800	0.5974	0.91-*N*	0.4365	0.0971	0.0195	0.0437	0.5968	0.2
11	0.5	0.95-*N*	0.4818	0.0299	0.0061	0.0770	0.5948	0.77-*N*	0.4351	0.1019	0.0180	0.0419	0.5969	0.3
12	0.25	1.07-*N*	0.4423	0.0098	0.0043	0.0792	0.5356	0.84-*N*	0.3901	0.0885	0.0166	0.0418	0.5370	0.3
13	1.0	1.86-*N*	0.5366	0.0212	0.0064	0.0953	0.6595	1.65-*N*	0.4827	0.1082	0.0189	0.0533	0.6631	0.5

the anode. It is conceivable that under such conditions ClO^- is electrolytically oxidized to ClO_3^- as follows:

$$ClO^- + 2O \rightarrow ClO_3^- \qquad (10)$$

The possible existence of such a reaction, considered as the *primary chlorate formation,* was suggested some time ago by Wohlwill.[10] However, experimental evidence directly substantiating such a reaction has not been available hitherto.

TABLE II.

Exp. No.	Total of escaped gases, expressed in equivalent quantity of oxygen	Oxygen, in grams corresponding to the consumed amount of current	Difference	Chlorate oxygen formed in the electrolysis, in grams	Quantity of oxygen corresponding to the free chlorine		Difference
					Computed from 1/3 of the chlorate oxygen	Found	
1	0.1474	0.1501	+0.0025	0.1143	0.0381	0.0397	+0.0016
2	0.1464	0.1494	+0.0030	0.1188	0.0396	0.0367	—0.0029
3	0.1460	0.1506	+0.0046	0.0946	0.0315	0.0316	+0.0001
4	0.1561	0.1540	—0.0021	0.1030	0.0343	0.0399	+0.0056
5	0.1506	0.1522	+0.0016	0.1051	0.0350	0.0411	+0.0061
6	0.0834	0.0847	+0.0014	0.0758	0.0253	0.0246	—0.0007

This reaction (10) was to be expected only in a hypochlorite solution that was as pure as possible to begin with, and especially free from chloride and rather strongly alkaline. Such a solution was prepared by adding a solution of hypochlorous acid, freshly distilled and freed from chlorine, to an excess of caustic soda solution prepared from metallic sodium. The resulting solution was electrolyzed with the same type of apparatus as was described above for hypochlorous acid (see page 25). The electrolyte between the two clay cups and the catholyte was concentrated sodium sulfate solution. The anode at first employed was again a cylinder of smooth platinum foil, having a surface area (one side) of 50 sq. cm. The quantity of electric current used, 0.25 amp. hr., was approximately the same in all of the experiments

[10] H. Wohlwill, Z. Elektrochem., 5, 57 (1898).

and was so chosen that, even in the most dilute solutions electrolyzed, there was free alkali and hypochlorite still present at the end of the individual experiment. The results of a series of experiments carried out in this manner, using 0.3*N* to 2.8*N* alkali and 0.4*M* to 0.7*M* sodium hypochlorite solutions, are presented in Table III.

In these experiments, chlorate and chloride appear as products of electrolysis in addition to oxygen. In order to permit direct comparison with the quantities of the other substances involved, the quantity of Cl^- is expressed in terms of equivalent oxygen.

TABLE IV.

Exp. No.	Difference between the oxygen corresponding to the current strength and that actually generated g.	Hypochlorite oxygen consumed g.	Chlorate oxygen formed g.	Chloride formed, expressed in the equivalent quantity of oxygen g.	Relation of the consumed hypochlorite oxygen to the chlorate oxygen formed and to the chloride oxygen formed
7	0.0411	0.0537	0.0821	0.0119	1.96 : 3 : 0.43
8	0.0472	0.0659	0.1006	0.0142	1.97 : 3 : 0.42
9	0.0350	0.0418	0.0649	0.0096	1.93 : 3 : 0.40
10	0.0363	0.0500	0.0752	0.0105	1.89 : 3 : 0.42
11	0.0351	0.0467	0.0720	0.0119	1.95 : 3 : 0.50
12	0.0374	0.0522	0.0787	0.0123	2.00 : 3 : 0.47
13	0.0420	0.0539	0.0870	0.0125	1.86 : 3 : 0.43

A glance at Table III shows that the result of electrolysis of the alkaline hypochlorite solution is materially different from that of the acid hypochlorous acid solution. In the latter, the Cl^- formed was discharged completely while now it remains in the electrolyte; previously the quantities of oxygen and chlorine discharged anodically correspond to the quantity of electricity passed, whereas now oxygen evolution lags materially behind that corresponding to the quantity of electricity consumed. In the acid solution, the hypochlorite-oxygen that disappeared was equal to the chlorate-oxygen formed; in the alkaline solution it is less than the latter, and the quantity of oxygen corresponding to the chloride-chlorine is no longer one-third the chlorate oxygen, but decidedly less. These relationships are brought out more clearly by Table IV.

The explanation of these phenomena may be sought in the simultaneous anodic discharge and anodic oxidation of ClO^- when the solution is alkaline; that is, reactions (7) and (10) take place concurrently. To what extent this is correct may be tested by computing from the quantity of oxygen corresponding to the chloride-chlorine, the extent of the anodic chlorate formation, the quantity of hypochlorite thereby disappearing and the quantity of chlorate oxygen formed, and by considering how much of the required hypochlorite came from primary chlorate formation, and how the observed deficiency of oxygen and the quantity of chlorate remaining for primary chlorate formation agree with the value calculated according to the hypochlorite requirement.

TABLE V.

Exp. No.	To anodic chlorate formation there are apportioned			To primary chlorate formation there are apportioned				
	Chloride oxygen formed, g.	Hypochlorite oxygen consumed, computed, g.	Chlorate oxygen, computed, g.	Hypochlorite oxygen consumed, g.	Chlorate oxygen formed, computed, g.	Chlorate oxygen formed, found, g.	Consumption of anodically generated oxygen, computed, g.	Consumption of anodically generated oxygen, found, g.
7	0.0119	0.0357	0.0357	0.0180	0.0540	0.0464	0.0360	0.0411
8	0.0142	0.0426	0.0426	0.0233	0.0699	0.0580	0.0466	0.0472
9	0.0096	0.0288	0.0288	0.0130	0.0390	0.0361	0.0260	0.0350
10	0.0105	0.0315	0.0315	0.0185	0.0555	0.0437	0.0370	0.0363
11	0.0119	0.0357	0.0357	0.0110	0.0330	0.0363	0.0220	0.0351
12	0.0121	0.0363	0.0363	0.0159	0.0477	0.0424	0.0318	0.0374
13	0.0125	0.0375	0.0375	0.0164	0.0492	0.0495	0.0328	0.0420

This has been done in Table V, which shows that the observed values at times are above and at others below those calculated and do not diverge too far from one another, especially when it is remembered that the values of Table IV already represent the differences between two determinations, and that the values computed in Table V thus represent the differences between differences and hence are affected to a relatively great extent by experimental errors.

In order to establish with absolute certainty that primary chlorate formation does occur, it was necessary to show that chlorate formation was the sole reaction in the electrolysis of a hypochlorite solution. Since this reaction becomes predominant

only in an alkaline hypochlorite solution, at a relatively low anode potential, it was to be anticipated that the goal might be attained by still further lowering the anode potential. The experiments of Table III were carried out with a smooth platinum anode. It seemed possible that by using a platinized anode, primary chlorate formation might take place without the anodic chlorate formation on account of the lower potential at such a platinized anode.

Accordingly, a hypochlorite solution 0.8*N* in free alkali, containing 0.146 g. hypochlorite in 50 cc. was electrolyzed for 15 min. at one amp., using a freshly platinized anode of the size previously employed. The current caused oxygen evolution solely, and the hypochlorite remained unchanged. Thus only the reactions,

$$2OH^- + 2 \oplus \rightarrow O + H_2O \qquad (9)$$

and $2O \rightarrow O_2$, took place; the potential consequently still was too low for chlorate formation.

Previous experiments had shown that prolonged oxygen evolution at a platinized anode causes its potential to rise continuously, and that an electrode given such preliminary treatment retains the increased potential imparted to it (even after the interruption of the current and transfer to another electrolyte) to such an extent that a new electrolysis may be started with it at an anode potential that is several tenths of a volt higher than with a freshly platinized anode. For example, at a freshly platinized anode, sodium sulfite can be oxidized only to sulfate; whereas, if the electrode is first polarized for several hours in caustic soda solution and then introduced into sulfite solution, its potential is 0.37 volt "nobler" and then sulfite is oxidizable not only to sulfate, but also to dithionate at more than 40 per cent current efficiency. The latter oxidation process requires a higher potential than sulfate formation.[11] A platinized anode may thus be adjusted to give certain oxidation products by means of a definite preliminary polarization.

Hence it was to be expected that at an anode, suitably prepolarized, primary chlorate formation would take place provided a potential could be attained which would not be so high (as would be the case with *smooth* platinum) that simultaneous dis-

[11] F. Foerster and A. Friessner, Ber. chem. Ges., 35, 2515 (1902).

charge of ClO^- would occur. This expectation was fully confirmed by experiment.

In Table VI are presented the results of two experiments in which the anode previously employed was platinized and then polarized anodically for several hours in dilute sodium hydroxide solution. For experiment 15 it was then used immediately; for experiment 14, after 24 hours' standing. In the latter case there

TABLE VI.

Electrolysis of NaOCl in Presence of NaOH.

Fifty cc. of electrolyte. Anode 50 sq. cm., anodically pre-polarized platinized platinum. Room Temperature. Current strength, 1 amp.

Exp. No.	Alkalinity of the solution before the electrolysis	Before the electrolysis there were present in the electrolyte			Oxygen corresponding to the amount of current consumed g	Total available oxygen g.
		Hypochlorite oxygen g.	Chlorate oxygen g.	Oxygen equiv. to the chloride g.		
14	1.03-*N*	0.4232	0.0220	0.0110	0.0771	0.5333
15	1.01-*N*	0.4177	0.0266	0.0074	0.0821	0.338

Exp. No.	Alkalinity of the solution after the electrolysis	After the electrolysis there were present in the electrolyte			Oxygen gas generated during the electrolysis g.	Total recovered oxygen g.	Loss of oxygen Per cent
		Hypochlorite oxygen g.	Chlorate oxygen g.	Oxygen equivalent to the chloride g.			
14	0.84-*N*	0.4089	0.0494	0.0093	0.0594	0.5277	1.2
15	0.81-*N*	0.4007	0.0617	0.0086	0.0586	0.5296	0.8

was an appreciable loss of oxygen charge which resulted from pre-polarization and hence a decrease in potential. As is seen, no chloride is formed at anodically pre-polarized, platinized platinum, and anodic formation of chlorate thus fails to occur; but hypochlorite and anodically formed oxygen are consumed and chlorate generated, and, as Table VII shows, the quantity of chlorate computed from the loss of anodically liberated oxygen agrees very well with that actually found.

In these experiments the alkali concentration of the anolyte decreased from 1.0*N* to 0.81*N* and 0.84*N*, respectively. Thus it remained strongly alkaline. This condition is essential to satis-

factory primary chlorate formation. When the initial electrolyte was about 0.1*N* in alkali, it became acid before the end of the run under conditions otherwise the same as those of experiments 14 and 15, and chlorate, now formed at greatly increased current efficiency, was produced along with chloride. Both anodic and secondary chlorate formation then took place at the platinized anode as was to be expected since both hypochlorous acid and ClO^- were in solution.

TABLE VII.

Exp. No.	Anodic oxygen consumed g.	Chlorate oxygen formed		Electrolytic efficiency of primary chlorate formation Per cent
		Computed g.	Found g.	
14	0.0177	0.0266	0.0274	23.0
15	0.0235	0.0352	0.0351	28.6

Thus it was proved that actual electrolytic oxidation of ClO^- to ClO_3^- is possible and that this oxidation is contingent upon the presence of free alkali and low anode potential.

Accordingly, in the electrolysis of a hypochlorite solution the following processes may occur *at the anode:*

(a) discharge of OH^- with the formation of oxygen gas;
(b) electrolytic oxidation of ClO^- to ClO_3^-;
(c) discharge of ClO^- forming ClO_3^- and Cl^-.

When the OH^- concentration is high, reaction (a) only takes place at the lowest potential possible. But if, due to oxygen evolution, the anode potential gradually increases, presently (b) takes place in addition to (a) and finally also (c), so that (a) is more and more repressed. Inasmuch as the potential required for (b) lies between that for (a) and that for (c), the range of potential over which this reaction with ClO^- is the only one is rather limited and the current efficiency comparatively low. In very low OH^- concentration, as in the case of an acid solution of HOCl, reaction (c) only occurs, and it is accompanied by

(d) a discharge of Cl^- to form free Cl_2 gas.

If the OH^- concentration lies between both extremes as in an initially weakly alkaline solution, then (a), (b), (c) and (d) occur, and as soon as the OH^- has been consumed in consequence of these reactions to such an extent that free HClO appears in addition to an excess of ClO^-, then

(e) the purely chemical action of HClO upon ClO^- takes place *in the electrolyte.*

IV. PROBABLE REACTIONS IN ALKALI CHLORIDE ELECTROLYSIS BASED ON THE EXPERIMENTS WITH HYPOCHLORITE ELECTROLYSIS.

If the electrolysis is started with a chloride solution which initially is free from hypochlorite, then, to the extent that the anode potential permits reaction (d) (the discharge of Cl^-) the ClO^- will soon share in the anode reactions, the ClO^- being produced by the reaction of the anodically liberated chlorine with OH^- formed at the cathode, but, being an anion, it is readily carried to the anode by the current. At the same time, reaction (b) can occur only in more strongly alkaline solutions of chloride. Hence, since reaction (d) is the one that determines the potential, and since its characteristic anode potential also suffices for (e), (b) cannot occur now without (c), and (b) will be repressed more and more in comparison with (c), the lower the initial OH^- concentration of the chloride solution. In a very weakly alkaline or in a neutral solution, (c) alone will be the hypochlorite-consuming and chlorate-generating process, until in a weakly acid solution reaction (e) will enter. In this way the above-described phenomena in the electrolysis of alkali chloride solutions are determined.

In a more strongly alkaline solution, in which the chlorine formed anodically is largely converted into ClO^- by the OH^- that is present in abundance close to the anode, it is possible for ClO^- and OH^- to exist at low concentrations only, in view of the materially lower potential at which these anions are acted on by the current. The electrolysis, therefore, must result solely in chlorate formation almost from the beginning, as experiment shows, and the current efficiency remains approximately constant as long as the chloride concentration does not decrease materially. If, on the other hand, a considerable concentration of ClO^- is

developed in an originally neutral chloride solution before stationary conditions have been reached in the electrolysis, then this can be due only to the fact that in this case the OH^- requisite for the formation of ClO^- are formed at an appreciable distance from the anode and that a concentration gradient of OH^-, and concurrently also of ClO^-, is developed between cathode and anode, whereby the concentration of these anions requisite for stationary conditions at the anode can become established through diffusion and convection only upon considerable enrichment of ClO^- in the electrolyte.

It was long believed that the evolution of gas from the electrodes thoroughly mixed the electrolyte, so that the concentration gradient mentioned could prevail only within the limits of a very narrow "diffusion layer," close to the anode. But only the cathodic hydrogen evolution is brisk from the start; the anodic evolution of oxygen is weak just at the time when the hypochlorite becomes plentiful. Hence there may be easily developed in the vicinity of the anode a thicker layer of solution, so that the marked concentration gradient of the ClO^- is spread over a greater distance. That this actually is the case becomes apparent if the electrolyte in chloride electrolysis is kept actively in motion. The results then are markedly different from those when the electrolyte is not stirred but merely undergoes the agitation due to gas evolution at the electrodes.

The following experiments carried out by A. Tenne shed light on this point. In these experiments a solution containing 4.345 mols NaCl per liter was electrolyzed between two concentric cylinders of small-mesh platinum wire gauze. The outer cylinder (height 5.3 cm. and diameter 4.5 cm.) served as anode; its surface, for the purpose of calculating the current density, may be assumed equal to the surface which the gauze can cover. The electrodes and 250 cc. of the electrolyte were contained in a glass beaker. This was closed tightly by means of a rubber stopper, through which were passed the current leads, a gas delivery tube, a tube for drawing off samples of the electrolyte, and the hermetically arranged stirrer guide. The stirrer, passing through the latter, was a glass rod situated at the axis of the two cylinders, and bent into a zigzag.

Experiments 16 and 17.

In these experiments, No. 16 and 17, the anode consisted of smooth platinum. It will be seen from Table VIII that with the electrolyte kept in rapid motion, equilibrium conditions are attained very soon after the electrolysis is started, *viz.*, while the hypochlorite concentration still is very low, and the current no longer produces anything except chlorate, which is formed at a current efficiency of about 66.7 per cent. But if the electrolyte is not stirred, the hypochlorite concentration rises to about four

TABLE VIII.

Experiments No. 16 and 17. 4.35 *N* NaCl; 10°; 1 amp.; D_A = 0.013 amp. 1 sq. cm; anode, smooth Pt.

Time after commencement of the experiment		The stirrer operates at 2,000 r. p. m.			The stirrer is not in operation		
hr.	min.	Anode potential, E in volts	Grams of hypochlorite oxygen formed in 100 cc.	Anodic generation of oxygen in per cent of the work done by the current	Anode potential, E_h in volts	Grams of hypochlorite oxygen formed in 100 cc.	Anodic generation of oxygen in per cent of the work done by the current
..	15	1.854	0.020	25.8	1.653	0.041	7.4
..	30	1.886	0.022	31.6	1.747	0.059	12.4
..	45	1.900	0.023	33.4	1.793	0.074	19.3
1	00	1.919	0.023	33.6	1.816	0.082	25.2
1	30	1.942	0.023	34.4	1.842	0.090	31.6
2	00	.....	.....	....	1.854	0.089	33.8
2	30	1.964	0.023	33.6	1.878	0.088	33.3
3	00	1.972	0.023	33.6	1.891	0.089	33.6
4	15	.....	.....	.....	1.921	0.089	33.6

times that observed in the first case, and the anodic evolution of oxygen reaches its equilibrium value, 33.3 per cent, much more slowly. At the same time, the anode potential rises far more slowly than in the first case, since it depends upon the current density at which the oxygen is evolved at the smooth platinum anode. Insofar as anode potentials can be reproduced at all at smooth platinum electrodes evolving oxygen, equilibrium is reached at approximately the same potential. Similar behavior is manifested at platinized anodes, as the following experiments, No. 18 and 19, show.

Experiments 18 and 19.

In addition to what has been discussed thus far, these experiments, recorded in Table IX, show another important effect of agitation of the electrolyte, and therefore of the hypochlorite, on the course of alkali chloride electrolysis. This effect is mani-

TABLE IX.

Experiments No. 18 and 19. 4.35-*N*, NaCl; 12°; 1 amp.; D_A = 0.013 amp./sq. cm. Anode platinized Pt, cathodically pre-polarized for 15 min. at 2 amp. in dilute sulfuric acid.

The stirrer operates at 1,750 r. p. m.				The stirrer is not in operation			
Time after commencement of the experiment hr. min.	Anode potential, E_h in volts	Grams of hypochlorite oxygen formed in 100 cc.	Anodic generation of oxygen in per cent of work done by current	Time after commencement of the experiment hr. min.	Anode potential, E_h in volts	Grams of hypochlorite oxygen formed in 100 cc.	Anodic generation of oxygen in per cent of work done by current
3	1.327	.....	....	2	1.361	.....	....
8	1.329	.....	....	7	1.359	.....	....
12	1.331	.....	....	10	1.357	0.034	2.6
15	1.334	.....	....	25	1.340	0.049	4.6
20	1.336	.....	....	30	1.336	.....	....
25	1.338	0.032	15.8	35	1.333	0.064	6.0
30	1.339	.....	....	40	1.332	.....	....
40	1.341	0.056	27.7	50	1.333	0.082	13.3
50	1.342	.....	....	55	1.333	.....	....
1 00	1.344	0.056	30.0	1 10	1.335	0.099	17.1
1 15	1.345	.....	....	1 25	1.336	.....	....
1 25	1.347	.....	....	1 30	1.336	0.106	24.4
1 40	1.348	0.056	34.6	1 45	1.337	.....	....
1 55	1.349	.....	....	1 50	....	0.116	28.2
3 00	1.354	.....	....	2 00	1.339	.....	....
3 10	.....	0.056	34.6	2 25	1.340	0.120	29.0
3 55	1.355	0.056	35.4	2 55	1.342	0.126	31.3
4 55	1.359	0.056	32.9	3 25	1.343	.....	....
5 25	1.358	.....	....	3 40	.....	.....	....
5 55	1.359	.....	....	3 55	1.344	0.130	32.7
6 25	1.360	0.056	34.7	4 25	1.344	0.130	32.8

fested by the changes that the anode potential undergoes during the passage of the current. As was determined long ago by Müller,[12] only a platinized anode shows a potential corresponding to the reversible discharge of Cl^-. The reversible potential of Cl_2 against a 4.34 *N* NaCl solution saturated with chlorine at 18°

[12] E. Müller, Z. Elektrochem., 6, 573 (1900); 7, 150 (1901); 8, 426 (1902).

is close to $E_h = +1.344$ volts. This value corresponds approximately to the anode potential at which electrolysis begins in Experiment 19 with the electrolyte at rest, correction being made for the current density. However, depolarization then sets in, the potential passing through a minimum and then slowly rising again.

This depolarization, which was mentioned above and which, even in an alkaline solution of chloride permits the early discharge of Cl^- at a potential considerably below the equilibrium value, depends on the following: The equilibrium potential of chlorine holds for solutions that are saturated with free chlorine at atmospheric pressure. At the very beginning of the electrolysis of a chloride solution, this condition may be regarded as existing even in the vicinity of the anode. In the course of the electrolysis, however, the ClO^- that gradually penetrates to the anode reduces the concentration of H^+ and therewith that of the free chlorine, the equilibria involved being indicated by the following equations:

$$Cl_2 + H_2O \leftrightarrows HOCl + H^+ + Cl^- \qquad (5)$$

$$ClO^- + H^+ \leftrightarrows HClO \qquad (4)$$

According to the formula

$$E_{Cl_2} = + \frac{0.0002T}{2} \log \frac{KC_{Cl_2}}{(C_{Cl^-})^2}$$

this means a decrease in the reversible potential of chlorine discharge. But if the electrolyte is vigorously agitated, ClO^- is brought to the anode immediately after the start of the electrolysis in quantity sufficient to bring about this depolarization immediately. In this case the anode potential therefore had, right from the start, the low value which it reaches only after a time in the case of an electrolyte that is at rest. The subsequent return to higher values depends on the well-known progressive polarization that platinum black always undergoes as the result of continued anodic evolution of oxygen. Since in the non-agitated solution this polarization outweighs more and more the initial depolarization, the latter attains its maximum much sooner than does the concentration of the hypochlorite, the depolarizer.

The effect of agitation on the concentrations of hypochlorite

attainable, and on anodic oxygen evolution, is especially noticeable if stationary conditions are allowed to develop in the agitated electrolyte, and the stirrer then stopped, or if the reverse is done. Experiments 20 and 21 were carried out in this way.

Experiments 20 and 21.

The hypochlorite concentration attained at the stationary state in a non-agitated electrolyte is higher than in the agitated; if the change is made from the former to the latter, then hypochlorite

TABLE X.

Experiments No. 20 and 21.

4.34-*N* NaCl, 0°, anode platinized, 1 amp., D_A = 0.013 amp./sq. cm.				4.34-*N* NaCl, 14°, anode platinized, 1 amp., D_A = 0.013 amp./sq. cm.			
Time after commencement of the experiment hr.	min.	Grams of hypochlorite oxygen formed in 100 cc.	Anodic generation of oxygen in per cent of the work done by the current	Time after commencement of the experiment hr.	min.	Grams of hypochlorite oxygen formed in 100 cc.	Anodic generation of oxygen in per cent of the work done by the current
Stirrer not in operation				*Stirrer operating at 1,300 r.p.m.*			
..	15	0.046	2.8	..	10	0.022	12.3
..	30	0.070	2.3	..	25	0.035	24.2
..	45	0.091	4.3	..	35	0.040	31.8
1	00	0.112	6.7	..	50	0.042	34.4
1	30	0.146	15.4	*Stirrer put out of operation*			
2	00	0.160	21.6	..	55	0.067	7.8
2	30	0.176	25.5	..	75	0.098	10.9
4	00	0.197	31.1	..	..	.....	....
6	30	0.204	34.1	..	..	.....	....
7	30	0.202	33.6	..	..	.....	....
8	00	*Stirrer put in operation at 1,800 r.p.m.*					
8	10	0.186	45.8	..	..	.....	....
8	30	0.173	44.9	..	..	.....	....
9	30	0.136	43.2	..	..	.....	....
10	30	0.104	38.2	..	..	.....	....
11	30	0.099	35.0	..	..	....	....

must disappear, that is, must be consumed more extensively by anodic chlorate formation than formed by the discharge of Cl^-. (Recorded in Table X.) Anodic oxygen evolution when the stirrer is started, goes considerably beyond 33.3 per cent current efficiency and then gradually settles back to this value while the hypochlorite concentration decreases. Conversely, if stationary conditions are reached in an agitated electrolyte, these do not apply for the electrolyte at rest; therefore, if the stirrer is stopped, the evolution of oxygen at once declines sharply and the hypochlorite concentration, which previously had become constant, again increases. Strong agitation of the elec-

TABLE XI.

Effect of Changing Design of Anode.

Amounts of hypochlorite oxygen obtained at the stationary state in 100 cc. electrolyte. No stirring.

	At a smooth anode g. O_2	At a platinized anode g. O_2
Using platinum wire gauze: Anode d. = 0.013 amp./cm² Solution 4.345*N* NaC- Temp. 10-12° C.	0.089	0.130
Using platinum foil: Anode d. = 0.014 amp./cm² Solution 5.0*N* NaCl Temp. 14° C.	0.340	0.540

trolyte consequently has an effect on the relation of the ClO^- concentration prevailing at the anode to that existing in the rest of the electrolyte similar to the effect of an adequate addition of free alkali to a chloride solution.

The difference in electrolytic behavior between a neutral and a rather strongly alkaline solution of alkali chloride is thus greatly lessened by vigorous agitation. Although hypochlorite solutions can be produced electrolytically and in a neutral chloride solution only, even then it is possible only if the procedure is such as to permit as great a difference as possible between the concentration of ClO^- in the electrolyte proper and its concentration close to the

anode. Everything that serves, on one hand, to maintain a certain concentration of free chlorine in the immediate vicinity of the anode as long as possible, and, on the other, to hinder the diffusion of ClO^- to the anode surface, will tend to increase the attainable hypochlorite concentration. High anodic current density, low temperature, and high chloride concentration all act in this direction, consistently with theory and experiment.

Furthermore, as the experiments just described show, it is necessary to eliminate as far as possible all factors that may interfere with the establishment of a steep concentration gradient of ClO^- between the main body of the solution and the layer immediately around the anode. The importance of this consideration was clearly recognized at an early stage in the technical production of bleach liquor, long before the theoretical interpretation was supplied by K. Kellner, who rendered valuable service in the construction of commercial apparatus. He announced that the obtaining of a "quiet anode layer" was absolutely essential for the efficient operation of the cells.

How sensitive the process of alkali chloride electrolysis is to changes in the design of the apparatus, changes that are apparently insignificant but really have a strong influence on the diffusion processes at the anode, is shown by the fact that under conditions identical in other respects, the attainable hypochlorite concentration at an anode consisting of a compact piece of platinum foil is much higher than that at a platinum wire gauze of the same active surface.[13] For this reason, the hypochlorite concentrations obtained with wire gauze anodes in an electrolyte not stirred (Experiments 17 and 19) are relatively low in comparison with those attainable at platinum foil electrodes, as Table XI shows.

The cause of this marked difference lies in the fact that with the wire gauze, which is subjected to the influx of ClO^- from all sides, the diffusion area is much greater than for compact platinum, toward which ClO^- can diffuse from one side only. Consequently, in the case of foil, a definite ClO^- concentration at the anode requires a far greater drop in concentration from electrolyte to anode than with gauze anode.

[13] P. Prausnitz, Z. f. Elektrochem., 18, 1034 (1912).

V. COMPARISON OF THE ELECTROLYSIS OF ALKALI CHLORIDE SOLUTIONS WITH THAT OF ALKALI BROMIDE SOLUTIONS.

An interesting side-light on the electrolytic behavior of hypochlorite solutions, so important to the interpretation of alkali chloride electrolysis, is the electrolysis of alkali bromide solutions. In bromide solutions, also, the current produces hypobromite at the start and later converts it to bromate; but at platinized anodes the anodic evolution of oxygen is very slight, especially in a concentrated bromide solution. The following experiment,[14] No. 22, is typical.

Experiment 22.

This experiment was carried out with a wire gauze anode in a vigorously agitated electrolyte, in a manner similar to Experiments 16 to 21; to prevent cathodic reduction, 0.2 per cent K_2CrO_4 was added to the electrolyte. The results are given in Table XII.

The potential of bromine against a 1 *N* KBr solution saturated with bromine at 25° is $E_h = +1.121$ volts. The anode potential

TABLE XII.

Experiment No. 22. 3.5-*N* NaBr; 10°; 1.6 amp.; $D_A = 0.021$ amp./sq. cm. Anode platinized, cathodically pre-polarized in dilute sulfuric acid, electrolyte stirred at 1,200 r. p. m.

Time after commencement of the experiment hr.	min.	Anode potential, E_h in volts	Grams of hypobromite oxygen formed in 100 cc.	Grams of bromate oxygen formed in 100 cc.	Anodic generation of oxygen, in per cent of the work done by the current
..	2	+1.011	.....	.....	...
..	5	+1.010	.....	.....	...
..	10	+1.007	.....	.....	...
..	13	+1.005	.....	.....	...
..	30	+1.004	0.099	0.026	1.9
1	00	+1.002	0.182	0.043	1.1
1	30	+1.001	0.276	0.056	1.1
2	00	.....	0.338	0.087	1.5
2	30	.....	0.400	0.120	0.8
3	00	.....	0.451	0.189	1.0
3	30	+1.001	0.498	0.230	0.8
5	00	.....	0.585	0.585	1.1
5	30	.....	0.597	.....	2.2
6	30	.....	0.618	0.743	1.5
7	30	.....	0.638	0.930	1.5
8	00	+1.001	0.638	1.026	1.1

[14] F. Foerster and J. Yamazaki, Z. Elektrochem., 16, 332 (expt. 19) (1910).

prevailing in this experiment therefore corresponds to the reversible discharge of Br^- to a solution, in the vicinity of the anode, which is only partially saturated with bromine. This is to be expected in view of the large solubility of bromine and its rapid rate of consumption in the strongly agitated electrolyte. The increase in hypobromite concentration exerts a slight depolarizing effect just as the hypochlorite did. In the present case, however, the depolarization persists until the conclusion of the experiment, because the amount of oxygen evolved is so slight as to possess no polarizing influence.

At this anode potential a process that gives rise to a strong evolution of oxygen, such as the anodic production of bromate in analogy with the anodic production of chlorate, is impossible in the approximately neutral electrolyte; accordingly, primary oxidation of hypobromite to bromate cannot occur either, although under other conditions, for example, in an alkaline solution, such a reaction has been demonstrated[15] to occur in hypobromite solutions. In spite of this the hypobromite is transformed, on progressive increase in concentration, into bromate. This can occur only through secondary bromate formation. This process is similar to reaction (3), thus:

$$2HOBr + BrO^- \rightarrow BrO_3^- + 2H^+ + 2Br^- \qquad (11)$$

and proceeds at a reaction rate which is 100 times greater than that of purely chemical *chlorate* formation. Consequently the concentration of free HOBr attained as the result of the establishment of the bromine hydrolysis equilibrium in the vicinity of the anode,

$$Br_2 + H_2O \leftrightarrows HOBr + H^+ + Br^- \qquad (12)$$

$$BrO^- + H^+ \leftrightarrows HOBr \qquad (13)$$

suffices, as the BrO^- concentration increases to bring about its conversion more and more rapidly into bromate until a balance between formation and consumption is again attained.

It is characteristic of such a reaction, which only gradually increases in velocity, that the hypobromite concentration tends to approach its equilibrium value slowly, and that the bromate

[15] H. Kretzschmar, Z. Elektrochem., **10**, 810, 811 (1904).

builds up to a considerable concentration long before the stationary state is reached. In chloride electrolysis, on the contrary, as was shown above, the electrochemical co-discharge of ClO^-, once it can set in, rapidly attains its stationary rate. This applies to cases where ClO^- can increase appreciably in concentration in the electrolyte, and where conditions approximating reversibility obtain, that is, at a platinized anode in a non-stirred electrolyte.

The difference in electrolytic behavior of alkali chloride and bromide solutions thus lies in the fact that in the case of the former the anode potential as fixed by Cl^- discharge permits even very small concentrations of ClO^- to take part in the *anode reaction* and be converted thereby into chlorate, oxygen being simultaneously evolved by the current. In the case of the bromide, however, the corresponding processes do not occur for BrO^- at the potential fixed by Br^- discharge, but the BrO^- becomes more and more concentrated until the rate of their *secondary conversion* into bromate, close to the anode, equals the rate of their electrolytic production. Thus it is that under comparable conditions, far greater concentrations of hypobromite develop in bromide electrolysis than of hypochlorite in the case of chloride electrolysis.

Since the purely chemical conversion of hypo-iodite into iodate, even in alkaline solution, takes place with far greater rapidity than the formation of bromate, when alkali iodide is electrolyzed at an anode density of 0.013 amp./sq. cm. and at anode potentials ranging from 0.53 to 0.57 volt, the stationary state is attained very quickly and at a very small hypo-iodite concentration (0.06 g./L. HIO) and iodate is produced almost exclusively by the current.

If chlorate were formed solely secondarily, that is, by purely chemical reaction, in chloride electrolysis, then, in view of the comparatively slow rate at which secondary chlorate formation proceeds in consequence of the low concentration of HOCl possible in close proximity to the anode, the hypochlorite would of necessity be able to attain a very much higher concentration in the electrolyte than the hypobromite. The fact that it is possible to obtain electrolytically only very limited concentrations of hypochlorite is due solely to the circumstances that at equal concentrations ClO^- is acted on by the current more readily than Cl^- or, at a given anode potential, ClO^- is acted on at a far lower concen-

tration than is Cl^-, being thereby decomposed and transformed into ClO_3^-. The latter anion, however, can take part in anodic reactions only at anode potentials far above those required for the reversible discharge of chlorine; in chloride electrolysis, therefore, it can become concentrated to a great extent before the current converts it into perchlorate.

Technische Hochschule,
Dresden, Saxony,
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THE PRODUCTION OF CHROMATES FROM FERRO-CHROMIUM ANODES.[1]

By M. deKay Thompson.[2]

From experiments by Y. C. Hsu, R. R. Ridgway, C. A. Norton and G. G. Kearful.

Abstract

The object of these investigations was to study the production of sodium chromate from ferro-chromium anodes under different conditions of current density, temperature, concentration of hydrate solution, and chromium content of anode, as has been done for permanganates from ferro-manganese anodes.[3] Results obtained on the effect of various factors on the current efficiency and the energy efficiency of the production of sodium chromate from ferro-chromium anodes are recorded. It was found that pure chromium anodes dissolve in sodium hydrate with 100 per cent current efficiency, but that this efficiency decreases with the addition of iron. The current efficiency in sodium carbonate solutions was about the same as in sodium hydrate, but the energy efficiency is better in sodium hydrate. There is no trouble with the skin effect, such as there is with ferro-manganese anodes. There is a minimum point in the current efficiency at 5 per cent sodium hydrate, which was found not to change with the current density or the anode composition. Chromium was never found in the anode mud. (About half of the manganese in ferro-manganese anodes goes into the mud.) The anode mud may be colloidal or non-colloidal. Low current density and high concentration of sodium hydrate favor the production of non-colloidal mud. Temperature is of no effect on current efficiency, but energy efficiency of course increases with temperature. At low current densities, below 5 amp./sq. dm., the

[1] Manuscript received June 16, 1924.

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[3] Wilson, Horsch and Youtz, J. Ind. Eng. Chem., **13**, 763 (1921); Thompson, Chem. Met. Eng., **21**, 680 (1919).

current efficiency is so high that the iron could not have been oxidized to the ferric state. There is a minimum current efficiency at about 5 amp./sq. dm. and a maximum at about 15 amp./sq. dm. In the case of ferro-manganese the current efficiency increases steadily with the current density.

I. PREVIOUS WORK.

As pure chromium is a limiting case of ferro-chromium, work on pure chromium anodes should also be mentioned. Hittorf was the first to investigate the behavior of chromium anodes.[4] According to Hittorf, depending upon the conditions, chromium goes in solution exclusively as divalent, as trivalent, or as hexavalent ions. In general hexavalent ions are formed, that is, the chromium is in the passive state. When used in the active form in the cell:

$$Cr \mid KCl \mid NaNO_3 \mid AgNO_3 \mid Ag$$

trivalent ions were formed. Trivalent ions were also formed when chromium was electrolyzed as anode in an absolute ethyl alcohol solution of zinc chloride. In some solutions at 100° C. and in some fused salts, chromium dissolved as anode to form divalent chromium ions.

These results could not be duplicated by Kuessner[5] using normal potassium chloride. He found that in all cases Cr^{6+} ions are formed simultaneously with Cr^{2+} or Cr^{3+} ions. Kuessner found also that an increase in temperature favored the formation of the lower states of oxidation, and that the current density was of no effect on the valence, between 8 and 0.06 amp./sq. dm. On electrolyzing alcoholic solutions of zinc chloride, the valence was not found to be constant, as stated by Hittorf.

None of the above experiments were with alkaline solutions. Previous to Hittorf's work Lorenz[6] published a two-page article describing briefly the production of potassium chromate in potassium hydrate from a ferro-chromium anode of "about equal content of iron and chromium." He also states that no iron goes

[4] Z. Phys. Ch., **25**, 729 (1898); **30**, 481 (1899); Z. Elektroch., **4**, 482 (1898); **6**, 6 (1899); **7**, 168 (1900).

[5] Z. Elektroch., **16**, 767 (1910).

[6] Z. anorg. Chem., **12**, 396 (1896).

in solution, but precipitates to the bottom of the cell. In 1898 Heibling[7] obtained a patent for this process, in which it is said that the anode must contain at least 55 per cent of chromium in order to make chromate. A patent for the same process was also granted to the Chemische Fabrik Griesheim Elektron.[8]

II. THEORY.

When a metal, which can exist in more than one state of oxidation, is polarized as an anode, theoretically it will dissolve in all the possible states in such amounts as to keep the corresponding electrode potentials equal; that is, in the case of chromium,

$$\frac{RT}{2F}\log\frac{P_{Cr^{++}}}{(Cr^{++})} = \frac{RT}{3F}\log\frac{P_{Cr^{+++}}}{(Cr^{+++})} = \frac{RT}{6F}\log\frac{P_{Cr^{6+}}}{(Cr^{6+})} \qquad (1)$$

Therefore

$$\left\{\frac{P_{Cr^{++}}}{(Cr^{++})}\right\}^3 = \left\{\frac{P_{Cr^{+++}}}{(Cr^{+++})}\right\}^2 = \frac{P_{Cr^{6+}}}{(Cr^{6+})} \qquad (2)$$

Since at constant temperature the electrolytic solution pressures P are constant, it follows that,

$$(Cr^{++})^3 = K_1(Cr^{+++})^2 = K_2(Cr^{6+}) \qquad (3)$$

as pointed out by Kuessner, and consequently certain amounts of all three ions should dissolve. Cr^{6+} ions do not exist to any measurable extent, but may be supposed to react with hydroxyl ions as follows:

$$Cr^{6+} + 8OH^- = CrO_4^{--} + 4H_2O \qquad (4)$$

consequently

$$(Cr^{6+}) = K_3\frac{(CrO_4^{--})\,(H_2O)^4}{(OH^-)^8} \qquad (5)$$

or since the concentration of water is constant:

$$(Cr^{6+}) = K_4\frac{(CrO_4^{--})}{(OH^-)^8} \qquad (6)$$

and therefore (3) becomes

$$(Cr^{++})^3 = K_1(Cr^{+++})^2 = K_2K_4\frac{(CrO_4^{--})}{(OH^-)^8}$$

Consequently if a chromium electrode is in equilibrium with a solution of its ions the concentration of CrO_4^{--} ions must be pro-

[7] Eng. Pat. 4,624. LeBlanc, The Production of Chromium and its Compounds, translated by Richards, p. 102 (1904).
[8] Germ. Pat. 143,320.

portional to the cube of the concentration of the divalent chromium ions, to the square of the concentration of the trivalent ions, and to the 8th power of the hydroxyl ion concentration. Since the concentration of the hydroxyl ions in a solution normal in OH^- ions is 10^{14} times that in a solution normal in H^+ ions, changing from normal acid to normal alkali would change the value of $\frac{CrO_4^{--}}{(Cr^{+++})^2}$, $10^{14} \times 10^8 = 10^{22}$-fold (not 10^{112}-fold as stated by Kuessner).

Chromium exists in an active and in a passive state, characterized by electrode potentials of 0.48 and 0.67 volt, respectively.[9] In the active state it dissolves readily as Cr^{2+} or Cr^{3+} ions like zinc and other electro-negative elements, but the value of the electrode potentials in this state is such that very few Cr^{6+} ions are required to satisfy equation (1). In the passive state, however, the electrode potential has moved (for some unknown reason) to the electropositive end of the electrolytic series. In this state it may be considered that the values of $P_{Cr^{++}}$ $P_{Cr^{3+}}$, $P_{Cr^{6+}}$, the electrolytic solution pressures of the ions, have all changed, but by amounts which make the electrode potential of Cr | Cr^{6+} the most electronegative of the three, and consequently hexavalent ions are the main product of electrolysis.

This seems a more definite and a more satisfactory explanation than that given by Le Blanc,[10] who refers the change in potential to a supposed change in the velocity of hydration of the ions, which amounts to assuming that the concentrations of the ions at the electrode are responsible for the large difference in electrode potentials in the two states. This would require a 10^7-fold change in concentration of the Cr^{2+} ions, which is unlikely, and moreover it does not take into account that the difference is due to some change in the metal itself. Foerster, in his "Elektrochemie wässeriger Lösungen" in discussing the passivity of chromium does not attempt to explain the anodic behavior of chromium in the two states by applying to this case the formulæ previously derived for the electrode potentials of metals existing in more than one state of oxidation.[11]

[9] Foerster, Elektrochemie wässeriger Lösungen, p. 415-16 (1922).
[10] Lehrbuch der Elektrochemie (1922), p. 325.
[11] Pp. 406 and 424 (1922).

In the case of pure chromium anodes, any deficit in current efficiency below 100 per cent would be due to the evolution of oxygen. With ferro-chromium there is also the possibility that the iron present would take part of the current to oxidize it to ferrate or to ferrous or ferric hydroxide, with a corresponding decrease in current efficiency. Lorenz's original paper states that no ferrate was formed, and this agrees with the following results. The upper limit of current efficiency will therefore be determined by the amount of iron in the anode. If a equivalents of Fe^{3+} are combined with one equivalent of Cr^{6+} then the limiting current efficiency would be $100/1 + a$ per cent. Three different samples of ferro-chromium were used, containing respectively 70.4, 68.0, and 78.75 per cent chromium, with a few tenths of a per cent of carbon. Assuming only chromium and iron are present, the corresponding maximum current efficiencies are 83.6, 82.0 and 88.8 per cent respectively, considering the rest of the current not used in producing chromate is used to oxidize iron to ferric oxide. If oxygen is also liberated, the current efficiency will be less than these values.

III. DESCRIPTION OF EXPERIMENTAL WORK.

Three different lots of ferro-chromium were used in these experiments. The first, containing 70.4 per cent chromium, was melted in a fire-clay crucible and cast into plates 12 cm. long, 4 cm. wide, and ½ to 1 cm. thick.

The second set of anodes was made by breaking a round ferro-chromium bar 5 cm. in diameter, containing 68 per cent chromium and 0.30 per cent of carbon. The bar was cracked into 15 cm. lengths by heating one side with an oxy-acetylene flame and then pouring water on the heated part. These were placed opposite a single sheet iron cathode in asbestos cloth in 1500-cc. beakers. Six beakers were connected in series in a galvanized iron trough, through which water circulated to keep the temperature constant, and six experiments were made at the same time. In some cases three identical runs were made to get better average values. In calculating the current density with these anodes half of the anode surface was considered active.

The third lot of anodes contained 78.75 per cent chromium

and a few tenths of one per cent of carbon. They were of rectangular cross-section of 1.5 by 5 cm. and 15.5 cm. long. Iron rods 6 mm. in diameter were cast in them for electrical connections. Both these and the 5 cm. rod were kindly furnished by the Electro Metallurgical Company of Niagara Falls through Mr. J. H. Critchett, to whom we express our sincere thanks. The rectangular anodes had a hard scale that had to be removed by an emery wheel before the first electrolysis. A sheet steel cathode wrapped in asbestos paper was placed on each side of an anode. Tall beakers were used as cells. The current was taken from a 110-v. circuit. In most of the experiments the quantity of electricity was determined by keeping the current constant during the run by an ammeter. In others a calibrated kilowatt meter was used, from which reading and the average voltage, taken from a recording voltmeter, the ampere-hours could be computed. Usually about 0.56 faraday was passed, corresponding to 10 amperes for 1½ hr.

TABLE I.

Anodes, 70.4 per cent FeCr. Two sheet iron cathodes in asbestos cloth diaphragms

Electrolyte, 1-*N* sol.	Na_2CO_3	NaOH
Duration, minutes	95.0	95.0
Temperature, ° C.	22-48	22-34
Current, amp.	3.0	3.0
Anode current density, amp./sq. dm.	10.0	10.0
Current efficiency in per cent	78.0	74.0
Na_2CrO_4 in g./amp.-hr.	0.79	0.75
Kw-hr. per Kg. Na_2CrO_4	8.60	6.93

The chromate content was determined by adding an excess of ferrous ammonium sulfate solution to an acidified sample of 10 cc. of the chromate taken after the mud settled, and titrating the excess of ferrous sulfate by permanganate. The analyses checked to a few tenths of one per cent.

It was found that the single determinations of current efficiency were frequently several per cent off the best representative curve. This is also true of similar determinations in making permanganate from ferro-manganese.

The first question investigated was the relative current and energy efficiencies in sodium hydrate and sodium carbonate solutions. The results are given in Table I; only one cell for each solution was used.

There is evidently not much difference between the two solutions as to current efficiency, but the lower resistance of the hydrate solution made the energy efficiency appreciably better. On account of this and the smaller heating effect in the hydrate solution, the following experiments were all confined to hydrate solutions.

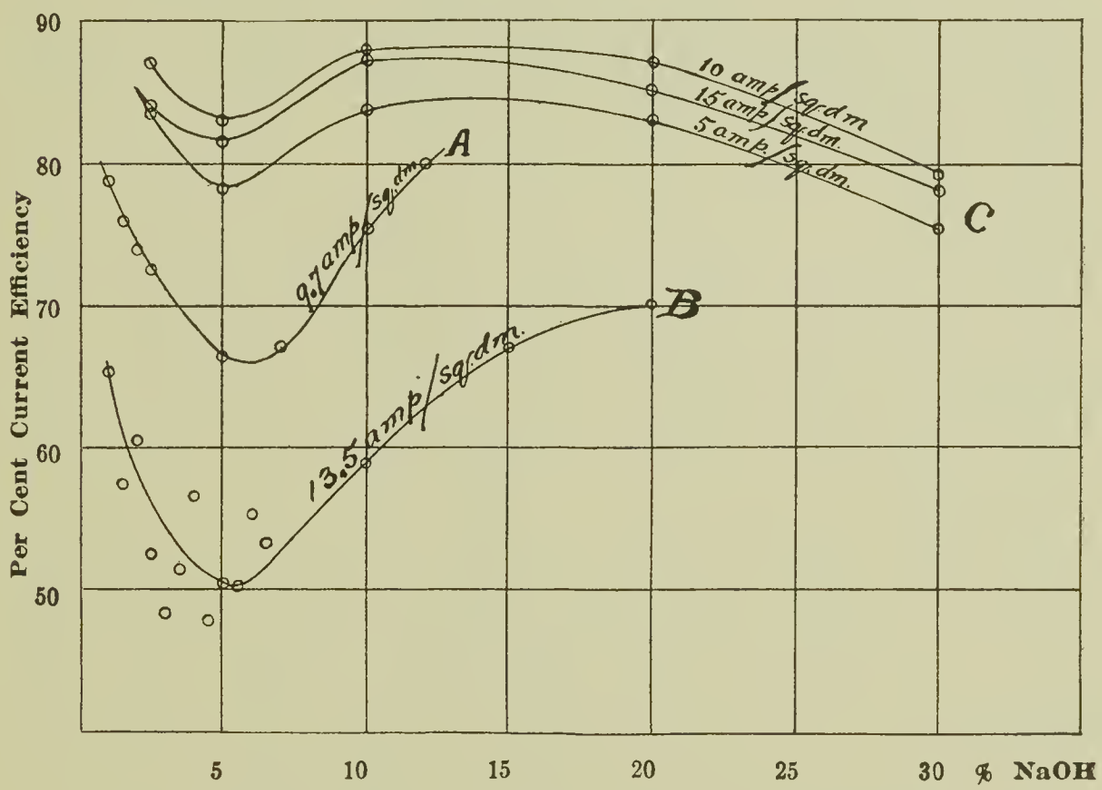

FIG. 1

Current Efficiency and Concentration of NaOH. Curves A and B, round anodes containing 68 per cent Cr; Curves C, rectangular anodes containing 78.75 per cent Cr.

IV. TEMPERATURE AND CURRENT EFFICIENCY.

Table II gives the results of three experiments at different temperatures, from which it is evident that any influence of temperature on current efficiency is not detectible. This agrees with the results of Kuessner in potassium chloride solutions, with pure chromium anodes. No insulating skin forms on these anodes at high temperature as it does on ferro-manganese anodes.

TABLE II.

Effect of Temperature Upon Current Efficiency.

Anodes, 70.4 per cent Cr. Solution, 1-*N* NaOH. Duration, 2 hr. 3.5 amp. Current density 10 amp./sq. dm.

Temperature, ° C.	21.0	40.0	85.0
Current efficiency, per cent ..	78.0	81.0	77.0
Kw-hr./kg. Na_2CrO_4	4.94	4.07	3.15

TABLE III.

Effect of Hydroxide Concentration on Current Efficiency.

Anodes: 5 cm. bars. Average of three separate determinations. Average deviation of a single determination of current efficiency = 2.2 per cent. 68 per cent Cr; I = 8.63 amp.; C. d. = 13.5 amp./sq. dm.; number of faradays passed, 0.557; duration 104 minutes.

Conc. NaOH in per cent	1	1.5	2	2.5	3	3.5	4
Current eff. ...	65.3	57.4	70.3	52.4	48.4	51.4	56.8
Volts	12.4	8.13	7.39	6.57	5.82	5.13	5.01
Kw.-hr. per kilogram	19.6	17.6	12.2	13.6	12.0	9.9	8.6
Conc. NaOH in per cent	4.5	5	5.5	6	6.5	15	20
Current eff. ...	47.9	50.2	50.1	55.3	53.1	67.1	70.6
Volts	4.44	4.99	4.53	4.13	3.86	3.40	3.56
Kw.-hr. per kilogram	9.2	10.0	9.0	7.4	7.3	5.1	5.0

NOTE: By per cent concentration is meant per cent NaOH referred to total weight of the solution.

V. CONCENTRATION OF HYDROXIDE IN SOLUTION AND CURRENT EFFICIENCY.

The curves in Fig. 1 and Table III show the relation between the concentration of the hydrate solution and the current efficiency. It will be observed that all curves show a minimum efficiency for 5 per cent solutions, independent of the current density and the composition of the anode. The three upper curves refer to anodes with 78.75 per cent chromium and were taken from

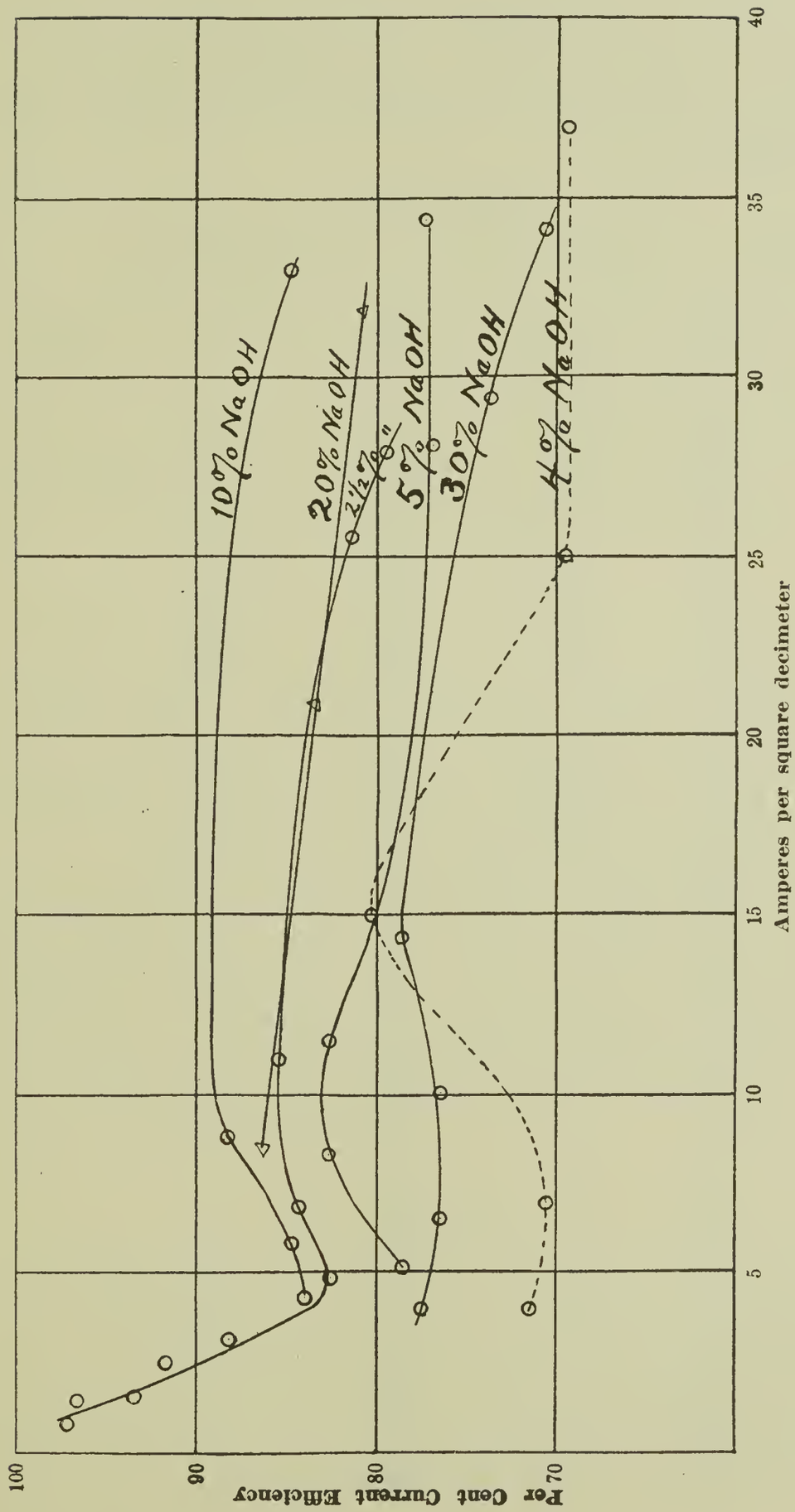

Fig. 2.

Current Efficiency and Current Density. Full lines refer to 78.75 per cent chromium anodes; the dotted line to 70.4 per cent chromium anodes.

Fig. 2. There is a corresponding minimum in the case of permanganate from ferro-manganese, but this comes at about 0.5 mol NaOH per liter or a two per cent solution. At higher concentrations of alkali the current efficiency falls below the values of this minimum.

TABLE IV.

Effect of Current Density on Current Efficiency.

NaOH Per Cent	Current density amp./dm.²	Kw-hr per kg. Na_2CO_3	Current efficiency Per Cent	Volts	Anode mud
2.5	0.80	1.85	97.1	2.87	non colloidal
	1.48	2.58	96.6	2.51	
	1.53	2.39	93.3	2.25	
	2.60	2.50	91.8	2.31	
	3.21	2.73	88.1	2.42	
	4.92	3.61	82.4	3.0	colloidal
	6.81	3.12	84.3	2.65	
	11.0	2.56	85.3	2.20	
	25.6	3.99	81.1	3.26	
	28.0	2.14	79.3	4.40	
5	5.22	2.74	78.4	2.16	colloidal
	8.29	2.64	82.3	2.19	
	11.4	3.46	82.7	2.88	
	28.1	3.40	76.7	2.63	
	34.3	2.94	77.0	2.28	
10	4.30	....	83.9	4.30	non-colloidal
	5.81	....	84.8	4.69	
	8.92	....	88.2	3.91	colloidal
	33.2	....	84.7	5.14	
20	8.51	....	86.1	....	
	20.9	....	83.3	....	
	33.7	....	80.7	....	
30	4.02	....	77.4	....	
	6.51	....	76.3	....	
	14.4	....	78.3	....	
	28.8	....	73.2	....	
	34.1	....	70.2	....	
4 (Anodes 70.4 per cent Cr)	4.0	....	71.3	....	
	7.0	....	70.2	....	
	10.0	....	76.2	....	
	15.0	....	80.0	....	
	25.0	....	69.2	....	
	37.0	....	69.2	....	

VI. CURRENT DENSITY AND CURRENT EFFICIENCY.

Fig. 1 shows that there is a marked decrease in current efficiency on changing from 9.7 to 13.5 amp./sq. dm. for the same anodes. Fig. 2 and Table IV give the results obtained with anodes containing 78.75 per cent chromium for different alkali concentrations and current densities, and one (dotted) curve for 70.4 per cent anodes in 4 per cent sodium hydrate. These curves deviate considerably from current-density, current-efficiency curves for permanganate, where the two increase together. The high values of current efficiency below a current density of 5 amp./sq. dm. in the 2.5 per cent solution, the only concentration in which such low current densities were used, indicate that the iron is not oxidized electrolytically to ferric hydroxide with 100 per cent efficiency below 5 amp./sq. dm. Consequently a larger proportion of current attacks chromium.

VII. COMPOSITION OF ANODE AND CURRENT EFFICIENCY.

Sufficient data to construct a curve of these variables were not obtained. However, Fig. 2 shows that, other conditions being equal, 78.75 per cent anodes have approximately a 10 per cent higher current efficiency than 68 to 70 per cent anodes. A run was made with a piece of pure chromium in 10 per cent sodium hydrate at about 45 amp./sq. dm., which gave 100.4 per cent current efficiency. The surface of the anode on removal from the solution was covered with a film of CrO_3, as shown by its turning green on heating. This would seem to indicate that the mechanism of the reaction is the oxidation of chromium to CrO_3 and the subsequent solution of this oxide by the hydrate, rather than equation (4) given above.

VIII. INSULATING FILM.

During the electrolyses no trouble was caused by the formation of an insulating film, which forms so easily on ferro-manganese anodes. Such a film can be produced, however, by allowing ferro-chromium to stand some time in a hydrate solution with 3 to 5 volts impressed on the cell. After standing in this way for two hours, application of 10 volts caused only the evolution of oxygen,

but 15 to 20 volts would break down the film and the anode would begin to corrode.

IX. MATERIAL EFFICIENCY.

No chromium was ever found in the anode mud, which shows the material efficiency was 100 per cent in all cases. This is quite different from the material efficiency of making permanganate from ferro-manganese, where a large part of the manganese goes into the mud as oxides.

X. NATURE OF THE ANODE MUD.

The anode mud occurs in two forms, one which readily settles to the bottom of the cell, and another which does not settle readily and which may therefore be considered colloidal. Which form the mud takes is determined by the concentration of the hydrate and the current density, possibly also by other factors, such as the composition of the anode. Low current density and high concentration of hydrate favor non-colloidal, easily filtered, mud. Thus with anodes containing 68 per cent chromium, a 5-per cent solution, and 9.7 amp./sq. dm. the mud was non-colloidal, but on increasing the current density to 20 amp./sq. dm. it was colloidal. With solutions containing less than 5 per cent hydrate at 9.7 amp./sq. dm. the mud was colloidal.

In 5-per cent hydrate at 5.2 amp./sq. dm. the mud from 78.75-per cent anodes was colloidal, which would indicate that the less the percentage of iron the greater the tendency to form colloidal mud. When the mud appeared in the colloidal form the anodes were bright, but when the mud was not colloidal they were covered with a film of oxide.

XI. CATHODIC REDUCTION.

The cathodes used in the runs given above were enclosed in asbestos cloth diaphragms. This was an unnecessary precaution, however, as is shown by the following experiments. A Pukall porous cup contained a sheet of platinum as anode. Outside the cup there was a sheet iron cathode, such as was used in the previous runs, dipping in the solution to be tested. Table V shows the other conditions. In no case was any loss in chromate found.

TABLE V.

Experiments on Cathode Reduction.

No.	Per cent conc. NaOH	Per cent conc. Na_2CrO_4	Amp./sq. dm.
1	5	10	5
2	10	5	5
3	5	5	10
4	5	5	20

XII. KILOWATT-HOURS REQUIRED PER KILOGRAM Na_2CrO_4 AT DIFFERENT CURRENT DENSITIES AND DIFFERENT CONCENTRATIONS OF NaOH.

Fig. 3 shows the relation between concentration of the electrolyte and kilowatt-hours per kilogram, but this would be shifted up or down by changing the distance between the electrodes. No

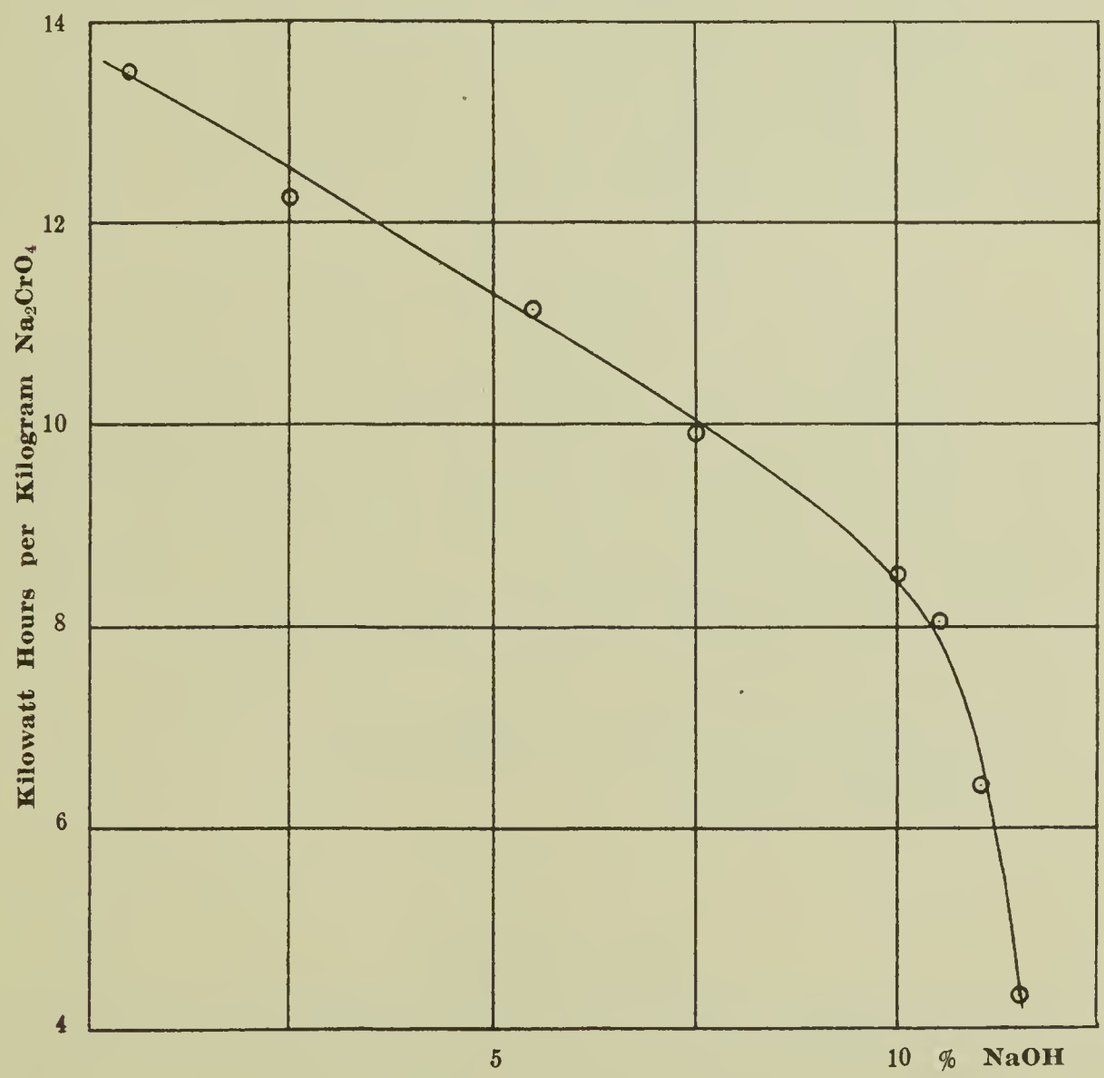

FIG. 3.

Kilowatt hours per kilogram of Na_2CrO_4. C. D. 9.7 amp./sq. dm. Round anodes, 68 per cent Cr.

relation can be found from these experiments between current density and energy yield, because the voltage change due to accidental differences in distance between the electrodes has a greater effect on the energy yield than changes in the current density itself, as is shown by the values of column 1, Table IV.

XIII. CONCENTRATION OF SODIUM CHROMATE AND CURRENT EFFICIENCY.

In the experiments so far described the concentration of sodium chromate never exceeded about 10 g./L., which would, of course, not be of any value in manufacturing chromate by this process. It would be necessary to know how the current efficiency changes with the concentration of the chromate, and whether it could be made sufficiently concentrated to crystallize on cooling. Some work has been done to answer these questions, but not enough to answer them fully. The little that has been done indicates that after the chromate has become more concentrated than 50 g./L. the current efficiency falls slowly. It is hoped that the study of this question will be taken up later.

XIV. COST OF $Na_2Cr_2O_7$ MADE BY THIS METHOD.

At the present price of chromium, 11.5 cents a pound in the form of ferro-chromium containing 4 to 6 per cent of carbon, and 3.5 cents a pound for 76-per cent sodium hydrate, the cost of materials for one pound of sodium chromate would be 6 cents, corresponding to 7.6 cents a pound for bichromate. As the price of sodium bichromate is 7.5 cents a pound, there are evidently no commercial possibilities in this process at present.

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DISCUSSION.

COLIN G. FINK[12] The forced electrolytic test for corrosion is very reliable whenever you want to determine whether or not an alloy is resistant to anodic corrosion. However, as a general test

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it is not applicable; you would certainly be disappointed in many of the chromium alloys. Professor Thompson's work is a good illustration. Even the high-ferrochromes, if used as anodes in alkaline solutions, will dissolve fairly readily. In acid solutions the anodic corrosion is even greater. And yet these very alloys when exposed to the atmosphere will stand up admirably well. Stainless steel, rustless iron and so on, all fall down on the anodic test. It is a pretty confirmation of the point brought out yesterday afternoon that you must not put your whole faith in the results of just one method of testing for non-corrodibility. Your method of testing should always conform, as nearly as possible, to the actual conditions of service to which the metal or alloy is to be put.

A paper presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 3, 1924, President Parmelee in the Chair.

THE AMPHOTERIC CHARACTER OF GELATINE AND ITS BEARING ON CERTAIN ELECTROCHEMICAL PHENOMENA.[1]

By Per K. Frolich.[2]

Abstract.

Electrochemical reactions involving gelatine (glue) are readily explained in the light of the modern knowledge of the physical chemistry of proteins. The mechanism of copper deposition from acid electrolytes containing gelatine is discussed in detail, and an explanation is suggested to account for the effect of gelatine as an addition agent in electrodeposition.

I. THE AMPHOTERIC CHARACTER OF GELATINE.

During the last few years our knowledge of the chemistry of the proteins has been greatly extended, through interrelated research in different branches of chemistry. Fischer's admirable studies of the structure of protein molecules, Pauli's work on the colloidal properties of gelatine, Loeb's physiological researches, as well as the extensive studies in leather chemistry by Proctor and Wilson, have brought the problems in this chapter of organic chemistry much nearer to solution. The decomposition of proteins by hydrolysis to form amino acids, together with Fischer's synthesis from simple amino acids of the octadecapeptide, which gives the biouret test for proteins, has established the view that the proteins themselves are complex amino acids of high molecular weight, probably from 5,000 to 15,000 or more. Loeb's elaborate studies of the physical chemistry of this group of organic compounds have proved that the proteins actually are amphoteric electrolytes.

[1] Manuscript received July 14, 1924.

[2] Research Assistant, Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Mass.

As a matter of simplicity we may use the following symbolic formula to designate the important characteristics of the protein molecule:

$$R\begin{cases}COOH\\NH_2\end{cases} \qquad (1)$$

where the large organic radical as well as the unknown numbers of acid and basic groups are indicated. When a protein comes in contact with an acid, the amino group will combine with the acid to form protein salt—for example, gelatine chloride, which may be written:

$$R\begin{cases}COOH\\NH_3Cl\end{cases} \qquad (2)$$

This gelatine chloride is dissociated like an ordinary salt, resulting in equilibrium between the undissociated salt and its ions:

$$R\begin{cases}COOH\\NH_3Cl\end{cases} \leftrightharpoons \left(R\begin{cases}COOH\\NH_3\end{cases}\right)^{+} + Cl^{-} \qquad (3)$$

On the other hand, if gelatine, or any other protein, be brought in contact with a base, the acidic character of the molecule will be prevalent, giving rise to the formation of a salt of the type:

$$R\begin{cases}COONa\\NH_2\end{cases} \qquad (4)$$

The sodium proteinate will dissociate to give a negative protein ion and a positive metal ion in equilibrium with the proteinate:

$$R\begin{cases}COONa\\NH_2\end{cases} \leftrightharpoons \left(R\begin{cases}COO\\NH_2\end{cases}\right)^{-} + Na^{+} \qquad (5)$$

As a protein never combines with an acid and a base at the same time, that is, never forms both types of salts simultaneously, it follows that the protein molecule under certain conditions must exist in an uncombined or neutral form, to which we gave the following formula:

$$R\begin{cases}COOH\\NH_2\end{cases} \qquad (1)$$

The condition necessary for the existence of this molecular type has been found to be a pH value of 4.7 for gelatine and a number

of other proteins. Thus, a pH value of 4.7 coincides with the iso-electric point of gelatine. From pH = 4.7 or less, that is, in solutions more acid than M/128 acetic acid, gelatine behaves like a base, giving rise to the formation of positive gelatine ions in the solution. Hence, if an acid solution of pH less than 4.7 containing gelatine be electrolyzed, the gelatine, or more correctly the gelatine ion, migrates toward the cathode. At a pH value of 4.7 no migration occurs, and the gelatine remains unaffected by the electric current. Similarly, at pH values greater than 4.7, that is, in faintly acid, neutral, and basic solutions, the gelatine will migrate towards and accumulate at the anode.

In the following discussion an attempt will be made to show how this amphoteric character of gelatine may appear helpful in throwing new light on several electrochemical reactions involving gelatine.

II. POLARIZATION OF ELECTRODES IN ELECTROLYTES CONTAINING GELATINE.

A number of investigators have studied the effect of gelatine on the polarization of electrodes, both with respect to gas evolution and the deposition of metals. Ch. Marie[3] and Thiel[4] found that the potential necessary to liberate hydrogen from an acid electrolyte was increased when gelatine was present, and Isgarischew and co-workers[5, 6], as well as Westrip[7], observed an increase in the cathode potential when gelatine was added to plain sulfuric acid electrolytes. In the Betts process for the electrolytic refining of lead, the metal is deposited from an acid electrolyte containing gelatine with a slight increase in polarization of the cathode.[8] The cathode potential is also increased by gelatine when copper is deposited from an acid solution.[9, 10, 11]

These observations are readily explained when it is considered that all the measurements are made with acid solutions, where

[3] Ch. Marie, Compt. Rend., 147, 1400 (1908).
[4] A. Thiel, Sitzungsber, d. med.-naturw. Ges. zu Münster, 1909.
[5] N. Isgarischew, Koll. Beiheft, 14, 25 (1921-1922).
[6] N. Isgarischew and S. Berkmann, Z. f. Elektrochemie, 28, 47 (1922).
[7] G. M. Westrip, J. Chem. Soc., 125, 1112 (1924).
[8] A. G. Betts, Trans. Am. Electrochem. Soc., 8, 64 (1905).
[9] M. LeBlanc, Elektromotorische Kräfte der Polarization (Abbh. d. D. B. G. No. 3), Halle, 1910.
[10] E. Müller and P. Bahntje, Z. f. Elektrokemie, 12, 317 (1906).
[11] A. Siewerts and W. Wippelmann, Z. f. anorg. Chem., 91, 1 (1915).

we have to deal with positively charged gelatine ions. The gelatine, on account of its positive charge, migrates to the cathode where it accumulates and offers additional resistance to the transportation of the inorganic cations up to the cathode surface, thereby increasing the cathodic polarization.[12] On the other hand, the anode potential would be expected to remain unaffected by an addition of gelatine to an acid electrolyte. This is confirmed by Isgarischew's observations.

Müller and Bahntje,[10] who studied the effect of gelatine on copper deposition, found that the texture of their deposits was changed when gelatine was added to an acid electrolyte, while in an alkaline cyanide bath the result was negative, as would be expected, because the gelatine migrates to the anode in an alkaline solution. The amphoteric character of gelatine also explains why Müller and Buchner[13] failed in their attempts to substitute gelatine for potassium chromate, in the formation of a cathode diaphragm to prevent reduction of hypochlorite in chloralkali electrolysis. As this cathode film is strongly alkaline, the gelatine is negatively charged and migrates in the opposite direction, that is, towards the anode. Hence, the gelatine cannot possibly accumulate to form a diaphragm around the cathode.

An interesting point is the time factor which enters into the electrolytic experiments with gelatine. Thus, Spear[14] and Wen and Kern[15] observed that copper deposited from an acid sulfate electrolyte containing gelatine or glue[16] changed its appearance "after some time." Furthermore, Newbery[17] states that it took a long time to reach the maximum of cathodic polarization when gelatine was added to an acid solution. He explained this result as being due to the necessity of the colloid (gelatine) penetrating

[12] That a layer or film of gelatine really is built up at the cathode can be seen if gelatine is added to an acid electrolyte (pH below 4.7). The increase in size of the hydrogen bubbles, as well as the difficulty with which they tear loose and escape, leaves it beyond doubt that we have to deal with a layer of extremely high viscosity next to the cathode. This local increase in viscosity must be due to an accumulation of gelatine, in agreement with the foregoing consideration.

[13] E. Müller and M. Buchner, Z. f. Elektrochemie, **16**, 93 (1910).

[14] E. B. Spear, C. Chow and A. L. Chesley, Eighth Int. Congr. App. Chem., **21**, 93 (1912); Trans. Am. Electrochem. Soc., **22**, 277 (1912).

[15] C. Y. Wen and E. F. Kern, Trans. Am. Electrochem. Soc., **20**, 121 (1911).

[16] Glue may be considered as being crude gelatine, the two substances having somewhat the same relation to each other as a commercial salt and the pure product. Therefore, it is unnecessary to distinguish between the two in discussing their electrolytic properties.

[17] E. Newbery, J. Chem. Soc., **105**, 2419 (1914).

into the pores of the metal before it could affect the overvoltage. However, a much simpler explanation is that the gelatine ion has to migrate to the cathode before any effect can be observed. As the current passes through the cell the gelatine gradually accumulates at the cathode, giving rise to a gradual increase in polarization, or to a gradual change in the appearance of the deposited metal (which will be discussed in the following section). Also, the polarization phenomena may be further complicated on account of the tendency of gelatine as an organic substance to undergo changes in chemical composition and physical properties, brought about by cathodic reduction with nascent hydrogen.

Working with pure sulfuric acid, Newbery observed that the cathodic overvoltage dropped gradually as the current density was decreased, while when gelatine was added to the solution the overvoltage remained constant in spite of a decrease in current density. The slow diffusing and viscous gelatine, which is already brought close to the cathode, remains there almost unaffected by a lowering of the current density, thus accounting for this observation.

Pring and Tainton[18] found that the current efficiency was increased by an addition of gelatine in the deposition of zinc from a strongly acid electrolyte, using a very high current density, 20 to 100 amp./sq. dm. This may be on account of the accumulation of gelatine around the cathode, thus slowing down the rate of diffusion, with consequent decrease in acid corrosion of the deposited metal.[19]

The effect of gelatine added to electrolytes has also been studied by several investigators, in connection with the so-called transfer-resistance, which originally was defined by Gore[20] as follows: "A species of electric resistance, distinct from that of polarization and of ordinary conduction-resistance, varying greatly in amount in different cases, exists at the surfaces of mutual contact of metals and liquid in electrolytic and voltaic cells." The validity of this statement has been doubted by Foerster,[21] and more re-

[18] J. N. Pring and U. C. Tainton, J. Chem. Soc., **105**, 710 (1914).

[19] Experimental work is now in progress in this laboratory to determine if the gelatine possibly may affect the relative ease of deposition of hydrogen and zinc ions, causing a preferential deposition of the latter, which would result in increased yield of deposited metal.

[20] G. Gore, Proc. Roy. Soc., **38**, 209 (1885).

[21] F. Foerster, Z. f. Elektrochemie, **17**, 881 (1911).

cently by Ferguson.[22] However, the theory has its defenders among English electrochemists, who claim that the transfer-resistance is increased, for instance, by gelatine.[23]

If we consider Gore's definition of this additional resistance, we will find that it may well fit in with the observations made on the effect of gelatine on cathode potentials in acid electrolytes, regardless of whether or not the transfer-resistance has any significance in the case of pure inorganic electrolytes. The resistance is simply a film or layer of gelatine overlying the cathode. This view is supported by the observation of Sand and Black,[23] that the transfer resistance is greatly decreased by increasing temperature when glue is present in the electrolyte. The higher temperature decreases the viscosity of the glue (gelatine) layer, and in turn facilitates the convection, diffusion, and migration of the ions to be discharged at the cathode. Hence, the transfer-resistance, or polarization, if we prefer to call it so, is decreased.

The fact that gelatine greatly increases the deposition potential, while the potential at rest remains unaffected, seems to have puzzled several investigators. However, this observation is readily understood when it is remembered that gelatine probably does not decrease the number of available inorganic ions in the electrolyte, and therefore cannot very well change the equilibrium potential determined by Nernst's equation. The change in potential will be observed when current is passed through the cell with consequent accumulation of gelatine at the electrode in question, as has been discussed previously.

III. ELECTRODEPOSITION OF METALS IN THE PRESENCE OF GELATINE.

From the preceding discussion it is obvious that the hydrogen ion concentration of the electrolyte is a most important factor in determining the behavior of gelatine during electrolysis. Furthermore, since gelatine and glue generally are added to an electrolytic bath for the purpose of exerting some specific effect on the process of cathodic deposition, it follows that a knowledge of the acidity (pH value) of the layer of electrolyte next to the cathode is necessary, in order to study the mechanism of the processes involved.

[22] A. L. Ferguson and G. V. Zyl, Trans. Am. Electrochem. Soc., 45, 311 (1924).
[23] H. J. S. Sand and T. P. Black, Z. phys. Chem., 70, 496 (1909).

That the acidity of this cathode film may be widely different from that of the main body of the electrolyte, has been shown. Thus, Thompson[24] reports that the cathode film in the deposition of nickel from an acid electrolyte may be less acid than the main body of the solution, and experiments in this laboratory have shown that for a certain zinc salt concentration a pH value of close to 6.2 existed next to the cathode, when the acidity of the electrolyte varied as widely as from pH = 6.2 to pH = 2.5.[25] These observations prove that we have two more or less independent variables, the pH value of the electrolyte and the pH value of the cathode film, which have to be considered in a study of the deposition of metals in the presence of gelatine or glue. Since the significance of the hydrogen ion concentration in electrodeposition has not been realized until quite recently, the data available regarding this factor are not many. Hence discussion has to be limited to only a few observations.

Deposition of Copper.

We will first try to picture the cathode processes in copper deposition from an acid electrolyte containing gelatine. This is of special interest, since acid copper electrolytes are extensively used in practice, and an addition of gelatine or glue is frequently made to the bath, especially in the electro refining of the metal. On account of the acidity of the electrolyte, considerably above that of neutral gelatine, the solution contains positive gelatine ions which consequently migrate towards the cathode. In addition to gelatine, hydrogen and copper ions serve as carriers of the positive current.

The copper ions are normally discharged at the cathode in such quantity as to account for the total current passed through the cell, since under ordinary conditions the potential does not increase sufficiently to liberate hydrogen ions. The hydrogen ions, which function as carriers of electricity up to the cathode, therefore remain there (of course, in equilibrium with an adequate number of negative ions, for instance $SO_4^{=}$ ions) and are only re-

[24] M. R. Thompson, Trans. Am. Electrochem. Soc., 41, 333 (1922).

[25] J. R. Eiffe (Graduate Thesis, Mass. Inst. Technology, 1924) observed that the pH value of pure zinc sulfate electrolytes always would approach 6.2 as the electrolysis proceeded. Thus, one may be justified in assuming that this is the acidity of the cathode film.

moved by convection and diffusion. The result is an accumulation of free acid next to the cathode, that is, in the cathode film.

The gelatine cations, as they approach the cathode, consequently enter into a region of increasing acidity, decreasing pH value. Hence the gelatine is carried next to the surface of the cathode where it remains, since its positive character prevents electric transference away from the acid cathode film, and the rates of convection and diffusion of this viscous substance are negligible. Between the copper cathode and the main electrolyte a layer of gelatine gel is therefore formed, the thickness of which depends on the quantity of gelatine added to the original electrolyte.

According to Loeb, a gelatine gel or solution may be considered as having a sponge-like structure, the long chain-like gelatine molecules symbolizing the solid framework of the sponge, while the voids are filled with the solvent in question. In our example the solvent consists of the acid copper sulfate electrolyte. As the current passes through the cell at constant rate, the electrolyte included in the film of gelatine gel will have a tendency to be depleted in copper ions. In the absence of gelatine new copper ions would have been brought into the cathode film by convection, diffusion, and migration.

However, when the sponge-like structure and high viscosity of the gelatine film are borne in mind, it will be understood that the convection, diffusion, and migration meet with an additional resistance, which must be overcome. The result is a decrease in the number of available copper ions at the seat of discharge, that is, at the cathode surface. An increase in deposition potential is to be expected, and such potential increases have been observed in the deposition of copper from an acid sulfate electrolyte, as mentioned in the preceding section. Furthermore, it is to be expected that the structure of the deposited metal will be altered under these conditions. Such a change in texture of the deposits, especially the production of a more dense and smooth metal, is just what is sought when gelatine (glue) is used as an addition agent in electrodeposition.

An explanation of the effect of gelatine as an addition agent in the electrodeposition of metals may be found if we combine the results of the above considerations with Blum's theory of the mechanism of crystal formation at the cathode. According to

Blum and Rawdon,[26] the conditions will be favorable to the formation of coarse crystalline deposits if an excess of metal ions be present next to the cathode, since the current will have a chance to select the easiest path, which results in continued growth of the crystals already present rather than the formation of new nuclei. This phenomenon is due to the fact that more energy is required for the formation of new nuclei than for the deposition of the discharged metal ions in the space lattice of a crystal. The essential conditions for the formation of smooth and fine-grained deposits are a low concentration of available ions, and a large reserve of undissociated salt, such as will be found in a solution of a complex salt like the double cyanide of silver or copper.

In an acidified copper sulfate electrolyte, the concentration of metal ions in close proximity to the cathode is relatively high, and, depending upon the composition of the electrolyte and the current density, there may be a tendency for a coarse crystalline deposit to be formed. If, however, gelatine (or glue) is present, a film of this substance will be built up next to the cathode. In order that the copper ions may be discharged, they have to migrate through the vacant spaces between the large gelatine molecules and discharge where they strike the cathode surface the moment they slip through the gelatine film. Thus, there will not be any chance for the formation of coarse crystals, since the gelatine film secures an even distribution of the copper over the cathode surface.

When the electrolyte is composed of a complex salt, the concentration of available metal ions is kept low as a result of chemical equilibrium, while in the above case we are dealing with a purely mechanical phenomenon, as it is the gelatine film of infinitesimal thickness which checks the number of copper ions coming into immediate contact with the cathode.

Loeb has shown that as the pH value decreases from 4.7 (isoelectric point of gelatine) the swelling, or the amount of water absorbed by a definite quantity of gelatine, increases, reaching a maximum at a pH value of 3.2. If the pH value is further lowered the swelling is again rapidly depressed. This means that the density of the gelatine film formed at the cathode is greatly dependent upon the prevailing pH value. At a pH value of 3.2 the

[26] W. Blum and H. S. Rawdon, Trans. Am. Electrochem. Soc., 44, 397 (1923).

swelling passes through a maximum which corresponds to a loose gelatine film, while on either side of this value the density becomes greater.

This fact may partly account for the apparent contradictions found in the literature regarding the behavior of gelatine as an addition agent in copper deposition. Thus, if the gelatine film becomes relatively thick or dense, depending upon the amount of gelatine added to the electrolyte and upon the pH value of the cathode film, a condition may well be arrived at where the transportation of the metal ions meets with so great a resistance as to force the copper to deposit in the voids of the gelatine gel. The gelatine is then gradually imprisoned in the copper deposit, and, hence disappears from the solution after a certain length of time.

This is what generally is called "co-precipitation" of the addition agent at the cathode. It explains why the solution is gradually deprived of the gelatine, and why organic matter is found in the deposited metal. However, the rate at which the gelatine is removed from the solution depends upon the copper salt concentration, the acidity of the electrolyte, the acidity of the cathode film, and upon the current density, as will be understood from the foregoing considerations. In practical work it may be sufficient to add gelatine or glue to the bath in slight amounts once a day or so, while certain laboratory experiments show that larger amounts of gelatine have been removed from the electrolyte in the course of about an hour.[10, 11, 27]

In order to avoid tiresome details, it may be sufficient to state that a comparison of the experimental conditions prevailing with the results reported confirms the explanation outlined above. While the introduction of gelatine in the deposit certainly will affect its appearance, the "co-precipitation" is not believed to be essential in order to improve the texture of the deposited metal. The main factor seems to be the regulating effect exerted by gelatine on the number of available metal ions, since zinc deposits may be entirely changed in their texture by gelatine, though they do not contain any organic matter whatsoever.

An extreme case of the so-called co-precipitation of gelatine with copper at the cathode is reported by Bancroft and Briggs.[28]

[27] G. Grube and V. Reusch, Z. f. Elektrochemie, **27**, 45 (1921).
[28] W. D. Bancroft and T. R. Briggs, Trans. Am. Electrochem. Soc., **22**, 287 (1912).

These investigators, who deposited copper from an electrolyte containing a very low concentration of copper salt and a relatively high percentage of gelatine, observed the formation at the cathode of what they called "gelatine-copper," a slippery film of gelatine containing copper in a very finely divided state.

Under similar conditions, except that the gelatine was left out, deposits consisting of numerous exceedingly thin needles more than one inch in length have been prepared in this laboratory. According to Blum's theory of the mechanism of cathodic deposition, such needle formation is due to a lack of metal ions in the solution next to the cathode. As was seen above, the effect of gelatine is further to decrease the concentration of copper ions at the seat of discharge.

The tendency to form needles will consequently be still more pronounced when gelatine is present in the electrolyte. At the same time, however, the free development of the needle structure is hindered because the deposition will be forced to take place in the voids of the dense gelatine film at the cathode. Hence, it is not surprising that the copper may be deposited in the gelatine gel in an extremely finely divided state, the dimensions of the haphazard needles or loosely adherent particles being of a magnitude sufficient to give rise to the color phenomena observed with colloidal metal, as reported by Bancroft and Briggs.

In this connection the experiments by Grube and Reusch[27] are of interest, showing that a periodical embedding of gelatine films in the copper deposit may take place under certain conditions. Thus, it was found that the gelatine under the prevailing experimental conditions was removed from the solution in a relatively short time, and that the microscopic examination of an etched cross section of the cathode indicated alternating layers of dense and loose metal.

The change in deposition potential as a function of time is shown in Fig. 1. Evidently the flat parts of the curve correspond to the normal deposition of copper. During the period of normal deposition, however, a film of gelatine builds up, causing a decrease in the copper ion concentration next to the cathode. The metal is finally forced to deposit in the voids of the gelatine gel, corresponding to the increase in deposition potential. On account of the infinitesimal thickness of the gelatine film, however, the

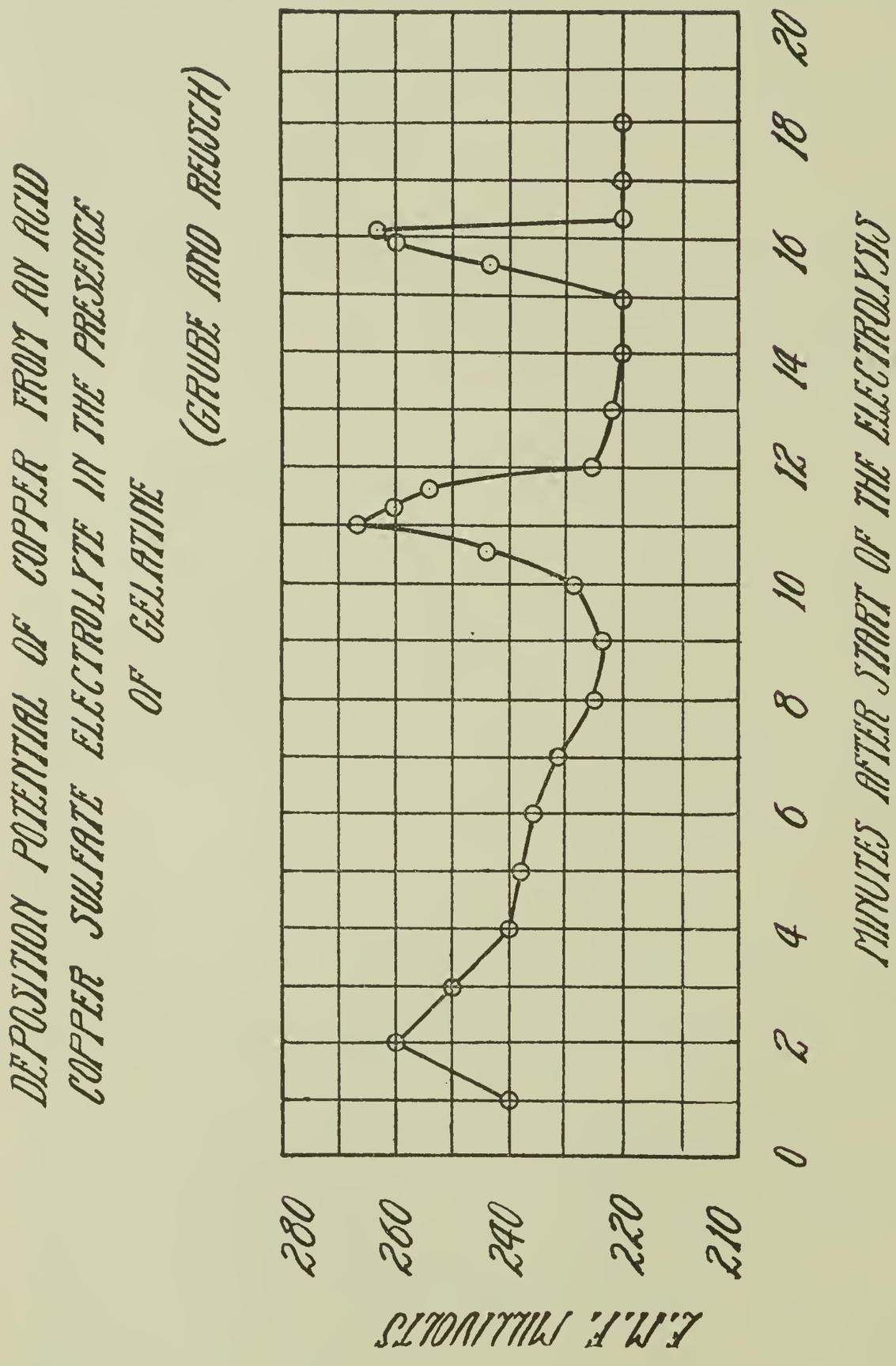

FIG 1. Change in Deposition Potential as a Function of Time.

deposit will soon have grown clear of it, and the normal deposition can continue for a certain length of time until a new film of gelatine is formed.

In this way the observed alternating layers of dense and soft metal, and the periodical changes in deposition potential, may be explained. On the other hand, the explanation offered by Grube and Reusch, that we have to deal with periodical crystallization of initially deposited colloidal metal, does not seem reasonable. The existence of an intermediate colloidal state in electrodeposition of metals has never been proved, and probably has no significance. This point has been discussed elsewhere by the author.[29]

Deposition of Zinc.

In zinc deposition, where gelatine also finds application as an addition agent, the problem becomes more complicated than with copper deposition. The free acid ordinarily present in a zinc sulfate bath causes the formation of positive gelatine ions, resulting in migration of the gelatine towards the cathode. As mentioned above, however, it has been found that the cathode film in the case of zinc deposition from a sulfate electrolyte has a pH value of about 6.2, and hence it does not seem probable that the gelatine can accumulate as close to the cathode surface as with the strongly acid cathode film of copper.

It is rather to be expected that in an acid zinc electrolyte a layer of gelatine forms at some (infinitesimal) distance from the cathode, where it may affect the cathodic deposition by regulating the concentration of available metal ions in a similar way as in the deposition of copper. On account of the aforementioned low acidity of the cathode film, which prevents the gelatine from coming in contact with the metal surface, one would not expect to find gelatine occluded in the deposited zinc.

In agreement with this view, it was impossible to detect any organic matter in six zinc cathodes deposited in the presence of gelatine from electrolytes ranging in pH value from 2.5 to 6.2, although the texture of these deposits in every case was more or less affected by the gelatine addition.[25] Hughes,[30] however, reports

[29] P. K. Frölich, Discussion of paper by V. Kohlschütter, Trans. Am. Electrochem. Soc., **45**, 240 (1924).

[30] W. E. Hughes, The Physics and Chemistry of Colloids and Their Bearing on Industrial Questions, Trans. Faraday Soc., **16**, part 3, 513; Appendix 130-131 (1921).

that he has found organic material in zinc which probably (!) had been deposited from a bath containing gelatine.

This may be due to high acidity of the electrolyte, causing so heavy an accumulation of gelatine at the cathode that some of it comes in contact with the metal surface, and is included in the deposit in spite of the high pH value of the cathode film. The fact that the gelatine gradually is removed from a zinc bath is probably due to hydrolysis and reduction by nascent hydrogen, rather than to "co-precipitation" at the cathode. The lack of experimental data, however, does not at the present allow definite conclusions in regard to the deposition of zinc.

Deposition of Nickel.

On account of the low acidity of the cathode film of nickel, a "co-precipitation" of gelatine would not be expected for the same reason as was pointed out above for zinc deposition. However, experiments showed that nickel deposited in the presence of gelatine appeared to be contaminated with organic matter. Upon dissolution of the metal in cuprammonium chloride and ferric chloride solutions a black residue was left.

A comparison of the photomicrograph of this residue, Fig. 2, with the photomicrographs in another paper by the writer,[31] shows that the residue caused by gelatine has a striking similarity to the residues of organic matter introduced in nickel deposits when carbonaceous gases were present in the electrolyte. It is probable that the mechanism of the reactions leading to contamination of the cathode is the same in both cases.

Thus (compare the conclusions drawn in the paper mentioned), the gelatine must have been decomposed by cathodic reduction to form gaseous products, which with nickel as a catalyst resulted in the formation of organic material in the deposited metal. If this were not so, that is, if for example the residue were simply a product of cathodic reduction of the gelatine itself, there would have been no reason why nickel should be contaminated and zinc not, since about the same cathodic conditions are prevalent in the deposition of the two metals. Zinc does not act as a catalyst with respect to the gas reactions in question, and hence is not affected by the decomposition products of the gelatine.

[31] This volume, page 87.

If any organic matter really is present in the zinc deposits, as reported by Hughes, then it must be in the form of gelatine, or slightly decomposed gelatine, since no residue can be detected by dissolving the metal. The same holds true for copper. Thus, no residue was found upon dissolution of copper deposited in the presence of gelatine and containing about 1 per cent organic matter. It is also interesting to note that Müller and Buchner[13] found an excess weight of copper deposits corresponding to 90 per cent of the weight of the gelatine added to their particular electrolyte.

CONCLUSION.

In the foregoing it has been shown that a great number of electrochemical reactions involving gelatine can be explained in the light of the modern knowledge of the chemistry of proteins. The data subjected to discussion were collected by a systematic review of the literature on the subject, and extended by the experimental work of the writer. All the data available have been considered, except the observation by Isgarischew and Westrip of a peculiar maximum in cathodic polarization when increasing amounts of gelatine were added to a sulfuric acid electrolyte. This phenomenon has not yet been fully explained, and it was thought advisable to leave it out of the discussion until further information has been obtained from the investigations now in progress in this laboratory.

The explanation suggested to account for the ability of gelatine or glue to improve the texture of electrodeposited metal, is the result of a combination of the modern theories in the field of protein chemistry with Blum's theory of the mechanism of cathodic deposition, and is merely a step forward along the same line of reasoning which has proved successful with all the other electrochemical observations discussed above.

It will lead too far to go into a detailed discussion of all the theories advanced to account for the effect of addition agents on the deposition of metals. Most of these theories are not based on experimental observations and are partly contradictory. Bancroft's idea of an adsorbed film of the addition agent at the cathode[32] is highly hypothetical,[33] The only attempt to corroborate

[32] W. D. Bancroft, Trans. Am. Electrochem. Soc., **23**, 266 (1913); **27**, 138 (1915).
[33] W. E. Hughes, Modern Electro Plating, London, 1924.

it by experimental results[34] failed to prove any adsorption of essential oils at metal surfaces, and Holmes and Child,[35] in working with gelatine as an emulsifying agent, could get no evidence of any concentration of gelatine at liquid-liquid interfaces (the optimum condition for film formation.)

The theory of a movable diaphragm does not seem sound, as it assumes migration of the discharged colloid in an electric field.[36] The idea of a reducing effect of a substance like gelatine, as proposed by Betts,[8] is not convincing. A theory which is especially interesting in this connection is the one which assumes the "co-precipitation" to be the essential factor, leading to improvement in texture of the deposited metal.

At first sight this theory might seem to be supported by the preceding discussions of the behavior of gelatine in the deposition of copper. However, as was outlined above, the acidity of a zinc-cathode film (pH = 6.2) will not permit of a continuous "co-precipitation" of gelatine at the cathode. It was also found that the texture of zinc deposits might be changed by an addition of gelatine to the electrolyte, although no organic matter could be detected in the metal. Furthermore, the negligible amount of addition agent used is against the theory.

Blum[36] has suggested that the addition agent might have the same effect in depressing the crystal growth as observed when alternating layers of different metals were deposited at the cathode. The observations with zinc do not support this view either. On the other hand, the explanation put forward in this paper to account for the effect of gelatine in electrodeposition of metals seems to agree with all the experimental data discussed.

The electrolytic property of an addition agent is a most important factor, which in the past has been overlooked. Some time ago the writer[37] called attention to the fact that nearly all of the substances used as addition agents possess electrolytic character. Carbon bi-sulfide was mentioned as an exception. How-

[34] F. C. Mathers and A. B. Lieble, Trans. Am. Electrochem. Soc., 31 271 (1917).
[35] N. H. Holmes and W. C. Child, J. Am. Chem. Soc., 42, 2049 (1920).
[36] W. Blum, Trans. Am. Electrochem. Soc., 40, 307 (1921); W. Blum and G. B. Hogaboom, Principles of Electroplating, New York, 1924.
[37] V. Engelhardt, Trans. Am. Electrochem. Soc., 21, 332 (1912).

ever, recent experiments in this laboratory[38] have shown that silver sulfide may be formed in silver cyanide plating baths to which carbon bi-sulfide has been added, in order to improve the texture of the deposited metal.

This observation also confirms the view that the effect of the addition agents is of an electrolytic more than of a colloidal nature. The accumulation of the foreign substance at the cathode with a consequent change in the concentration of the available metal ions, seems to be essential.

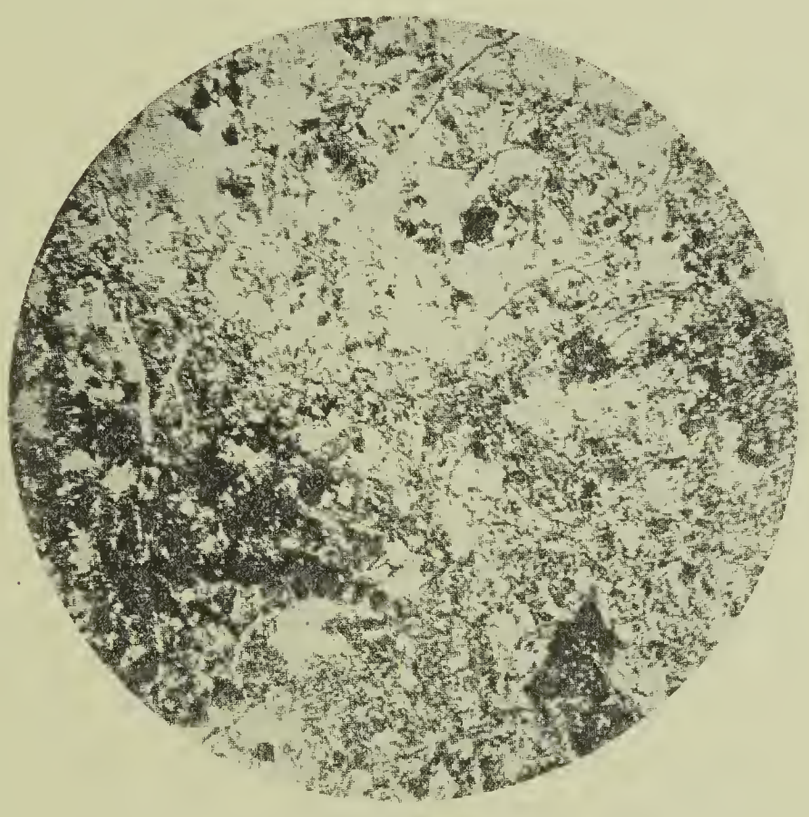

Fig. 2. Organic matter included in nickel deposited from an acid electrolyte containing gelatine. (x 22)

In a later paper it will be shown that such a change in metal ion concentration may be effected in different ways. In the present discussion only gelatine has been considered, while other substances known to be effective as addition agents in electrodeposition have been left out entirely. The different addition agents vary so widely in their chemical and physical properties, that only a detailed study of each one of them separately can be expected to throw light on the mechanism of the reactions involved.

[38] A. R. Thatcher, Graduate Thesis, Mass. Inst. Technology, 1924.

DISCUSSION.

R. J. McKay[39]: What is the best commercial pH for depositing zinc from zinc sulfate solutions? How does it compare with that of nickel sulfate solutions?

W. Blum[40]: I will make a prediction, without having made any measurements, that the best pH at the current densities that are ordinarily used in zinc plating in sulfate solutions is probably between 2 and 4. One of the difficulties in zinc plating is that the anodes are dissolving chemically all the time, and sulfuric acid is added at least once a day; hence it is pretty safe to say that in an ordinary zinc plating bath the pH may vary as much as from 2 to 5 in a day.

R. J. McKay: Then, founded on that, I would like to suggest to Dr. Frölich that part of the mystery indicated by the use of the term catalysis might be cleared up by the study of the hydrogen ion concentration. That is, you have these two metals, copper and zinc, with which you get good results by the addition of gelatine. The solutions are both high in hydrogen ion concentration. For depositing nickel the concentration is lower, and the hydrogen ion concentration, according to your findings, affects the position and the density of the gelatine film.

F. C. Mathers[41]: Granting that gelatine is carried to the surface of the cathode, where it produces a film, why does it not produce the same film on all cathodes and thereby have the same effect with each and every metal? A different effect is obtained with glue in different baths. A different effect is even produced by glue with the same metal by merely changing the acid radical with which the metal is combined. In a lead fluosilicate bath the glue goes to the cathode and produces a smooth deposit. In a tin fluosilicate bath the glue should go to the cathode as before, but in this case the deposit is not smooth. A satisfactory addition agent for a tin sulfate bath is entirely unsatisfactory for a tin chloride bath. The theory of Dr. Frölich does not take these experimental facts into consideration. Therefore, I think that a broader theory than that presented in this paper is necessary.

[39] Supt. of Technical Service, International Nickel Co., New York City.
[40] Chemist, Bureau of Standards, Washington, D. C.
[41] Prof. of Chemistry, Univ. of Indiana, Bloomington, Ind.

W. BLUM: I believe that this paper may be considered as one of the few broad generalizations on the effect of amphoteric colloids, such as gelatine, upon electrodeposited metals. Certainly some of the differences that Dr. Mathers has referred to may be accounted for by differences in the hydrogen ion concentration of his particular tin or lead baths, which, as Dr. Frölich has shown, may determine whether the glue will go to the cathode or to the anode. The effect of the anion may involve the potential relations. If we plot the current density against the potential for any metal such as nickel or iron from a chloride solution, we may have a curve showing only slight polarization; if we have a sulfate solution, we may have a curve with greater polarization, and if we have a complex solution, or one to which we have added an organic acid, we may have a curve with marked polarization. The question as to whether the colloids will be carried to the cathode or not depends principally on the hydrogen ion concentration of the solution, which also affects the position of these curves; but whether they are included in the cathode may depend upon whether a potential can be reached at which the colloid can be changed into some substance, whatever it may be, that actually enters into the deposit.

In a recent paper by W. E. Hughes upon the effect of gelatine in zinc sulfate solutions,[42] it was found that in a solution of zinc sulfate to which no acid was added the gelatine had practically no effect upon the structure of the deposit, but it did cause foaming at the anode. On the other hand, if the solution was acidified with sulfuric acid, the gelatine did have a marked effect upon the structure of the deposit. Mr. Hughes did not make any hydrogen ion measurements but he tested the solutions with congo red with results indicating that in the two solutions the pH was respectively above and below 4, the iso-electric point of gelatine. Dr. Frölich's theory shows that gelatine will not go to the cathode unless the pH is less than 4.7, and that it goes to the anode when the pH is more than 4.7. Mr. Hughes' paper is therefore a striking confirmation of Dr. Frölich's theory.

E. M. BAKER[43]: With regard to the pH in a zinc plating bath of the sulfate type, our own measurements, using methyl red and

[42] The Metal Industry (London), 25, 269 (1924).
[43] Asst. Prof. Chem. Eng., Univ. of Michigan, Ann Arbor, Mich.

phenol blue indicator in an acid zinc sulfate solution, showed the best results with an unagitated solution at an estimated pH of about 4.6. On the other hand, we have other evidence to lead us to believe that the acidity is much less at the actual cathode surface for good deposits. For example, in barrel plating we found that unless the solution was so alkaline that it was actually milky, containing precipitated aluminum hydrate or zinc hydrate, that good deposits could not be obtained.

F. C. Mathers: The solutions I had in mind when I was referring to tin and lead are all strongly acid, from 2 to 10 per cent free acid.

Per K. Frölich: Regarding the point brought up by Dr. Mathers, in the present paper tin and lead electrolytes have not been considered because the necessary experimental data, such as have been given for the case of copper, have not yet been obtained. It is our plan, however, to complete the work started on zinc deposition, and also to include tin and lead electrolytes in the study of gelatine as an addition agent.

The explanation suggested for the effect of gelatine on copper deposition can not be generalized directly, but the underlying principle, Blum and Rawdon's theory of cathodic crystal formation, may be a general one. Judging from available data, this does not seem impossible.

A paper presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 3, 1924, President Parmelee in the Chair.

THE INTRODUCTION OF CARBONACEOUS MATTER IN ELECTRODEPOSITED IRON AND NICKEL.[1]

By Per K. Frölich.[2]

Abstract.

It has been definitely shown that carbonaceous matter may be found in electrodeposited iron and nickel, when there is not the slightest indication of any organic colloid in the electrolyte from which deposition takes place. Salts of organic acids or carbonaceous gases dissolved in the electrolyte are in many cases sufficient to account for the contamination of the deposited metal with carbonaceous matter. It is even possible to introduce such impurities into absolutely pure electro deposits of iron and nickel, by exposing these deposits to cathodic polarization in solutions containing nothing but organic salts or carbonaceous gases plus an inorganic conductivity salt. The reactions responsible for the contamination are more or less dependent upon the nature of the inorganic ions discharged at the electrodes.

INTRODUCTION.

A phenomenon frequently met with in electrodeposition is that the metal deposited at the cathode appears to be contaminated with some foreign material (not including other metals). Such impurities generally are of organic basis, although in some cases they may be inorganic in character (metalloids). The source from which the organic contaminations are derived may be organic salts dissolved in the electrolyte, more or less insoluble matter liberated by the dissolution of an impure metallic anode, contaminations from the air, or they may be caused by the so-called "addi-

[1] Manuscript received July 8, 1924.

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tion agents," which are sometimes added to an electrolytic bath in order to exert some specific action on the process of cathodic deposition.

The object of the research presented in this paper was to study the significance of colloidal reactions in the processes leading to contamination of iron and nickel, when organic materials were dissolved in the electrolyte from which deposition occurred.

Iron and nickel were chosen for the investigation since these metals were already known to be contaminated when deposited from electrolytes containing organic matter, but containing no primary colloids. The following experimenters have found carbon[3] present in iron electrodeposited from oxalate electrolytes: Avery and Dales[4,7] (in a study of Classen's method of analysis of iron), F. P. Treadwell and Christie,[5] and Skrabal.[9] Verver and Groll[6] did not find any carbon, but later the former[8] observed that the impurities are first introduced into the cathode after all the metal has been deposited from the oxalate solution. That iron is contaminated by carbonates has been reported by Verver,[8] and by formic and acetic acids by Ehrenfeld.[10] Lambris[11], Fischer and Lambris,[12] W. D. Treadwell,[13] and F. P. Treadwell[14] report similar contaminations in nickel deposits. Foerster[15] and Madsen[16] call attention to the presence of organic material in iron and nickel electrodeposited from inorganic electrolytes on a commercial scale.

Various explanations and theories have been offered as to the nature and causes of carbonaceous contamination in electrodeposited metals of the iron group. Of these the following are examples: Carbon is present as carbide (Verver[8]); organic acid

[3] The term "carbon" is here used in the same sense as in the original papers quoted, that is, simply to designate the organic impurities, regardless of their chemical composition.

[4] S. Avery and B. Dales, Ber., **32**, 64 (1899).

[5] F. P. Treadwell, Kurzes Lehrb. d. anal. Chemie, 7th ed., Vol. II, p. 518.

[6] H. Verver and F. Groll, Ber., **32**, 806 (1899).

[7] S. Avery and B. Dales, Ber., **32**, 2233 (1899).

[8] H. Verver, Chem. Ztg., **25**, 792 (1901).

[9] A. Skrabal, Z. f. anal. Chem., **42**, 395 (1903).

[10] S. Ehrenfeld, Ber., **38**, 4139 (1905).

[11] G. Lambris, Z. f. Elektrochemie, **15**, 973 (1909).

[12] A. Fischer, Elektroanalytische Schnellmethoden, p. 167 (1908).

[13] W. D. Treadwell, Elektroanalytische Methoden, p. 143 (1915).

[14] F. P. Treadwell, *l. c.*, p. 115.

[15] F. Foerster, Abbh. d. Bunsen. Gesellsch., **2**, 77, 78 (1909).

[16] C. P. Madsen, Trans. Am. Electrochem. Soc., **45**, 249 (1924).

radicals (*e. g.*, oxalate) are reduced to carbon, which is deposited simultaneously with the metal (Avery and Dales, *l. c.*); oxalic acid is reduced at the cathode to glyoxyllic acid, followed by oxidation to colloidal sludge at the anode, migration to the cathode, and co-precipitation with the metal (Foerster[15,17]).

The theory of colloidal co-precipitation from commercial electrolyte (Foerster[15]) is supported by Madsen (*l. c.*), who states that the "cold-short" phenomenon exhibited by nickel is due to deposition of organic colloids on intercrystalline facings causing rupture of the crystal bondage when expanded by heat. On the other hand, this view is opposed by the early work by Skrabal (*l. c.*) showing that carbonaceous matter, liberated by the dissolution of an anode consisting of contaminated oxalate-iron, will not be deposited again at the cathode. Lambris (*l. c.*) claims that the introduction of carbonaceous matter in the cathode is due to gas reactions in which acetylene, produced by cathodic polarization, is an essential intermediate step.

Apart from obvious discrepancies between different investigators, a study of the literature on the subject shows that sufficient experimental data are not available to permit of definite conclusions as to the mechanism of the reactions leading to contamination of the deposited metal. Hence, it was thought desirable to extend the study of the phenomenon, the scope of the investigation being primarily to get definite information as to the role played by colloids in these reactions.

EXPERIMENTAL PART.

The metal deposited was tested for carbonaceous matter by Classen's method,[18] using a combined treatment with a cuprammonium chloride solution and a solution of ferric chloride. In this manner the iron or nickel is brought into solution leaving any organic impurities unattacked. This method was used in preference to a direct treatment with acids, which might have been expected to affect the organic matter through reduction by nascent hydrogen. A number of blanks showed that quantitative dissolution took place when iron or nickel was deposited from electrolytes containing nothing but the pure salts of the metals in question.

[17] F. Foerster, Elektrochemie w. Lösungen, 2d ed. (1915); Z. f. angew. Chemie, 19, 1847 (1906).

[18] A. Classen, Quant. Anal., 4th ed., p. 244.

TABLE I.

Deposition of Iron in the Presence of Organic Matter

The experimental conditions are described on page 91.

No.	Composition of Electrolyte g./L.	Current Density amp./dm.²	Time hr.	Metal Deposited g.	Type of Residue
2	17 g. ferrous amm. sulfate. 50 g. amm. oxalate.	1.5	14	0.52	Small quantity of black, spongy flakes.
4	8 g. ferrous chloride. 60 g. amm. oxalate.	1.5	28	0.42	No residue.
61	535 g. ferrous chloride. 20 g. amm. acetate. Free acetic acid.	1.5 to 2.0	24	About 0.25	No residue.
62	535 g. ferrous chloride. 12 g. citric acid.	1.5 to 2.0	24	About 0.25	No residue.
12	Ferrous sulfate saturated at 20° C. Illuminating gas.	2.0	20	3.76	Negligible quantity of black flakes.
11	535 g. ferrous chloride. Illuminating gas.	2.0	20	6.32	As in No. 12.
16	535 g. ferrous chloride. Illuminating gas.	2.0	20	1.54	Negligible amount as in No. 11 and 12.
22	Ferrous amm. sulfate saturated at 20° C. Illuminating gas.	2.0	20	1.88	About 30 mg.—much more than in runs 12, 11 or 16.
13	535 g. ferrous chloride. Acetylene.	2.0	5	0.84	0.0086 g. organic matter = 1.02% of total deposit.
20	535 g. ferrous chloride. Diaphragm around anode. Acetylene in cathode compartment.	2.0	20	11.04	0.0425 g. residue = 0.41% of total deposit.

1. *Deposition of Iron and Nickel in the Presence of Organic Matter.*

The results of a series of experiments made on electrodeposition of iron and nickel, when different kinds of organic materials were present in the electrolyte, are given in Tables I and II.

The electrolytes were made up of distilled water and salts of the highest purity, varying in volume from 250 to 300 cc. Platinum foil, 0.35 sq. dm. in area, was used for cathodes. The anodes consisted of platinum wire. Gases when used were bubbled in from the bottom of the cell near the cathode. In all the experiments the temperature was kept between 25° and 28° C. The last column refers to the observations made when dissolving the deposits according to Classen's method described above.

Quantitative determinations of the residues were only made in a few cases, since the substance left after dissolving the metal would be unfitted for microscopic examination when dried down to constant weight.

Summary of Results. The results may be briefly summarized as follows:

Ammonium oxalate causes contamination of iron in the case of a complex oxalate electrolyte prepared from ferrous ammonium sulfate, but not when ferrous chloride is used. That oxalate gives rise to introduction of organic matter in the cathodic deposit from a complex solution of nickel salts, as used for electroanalysis, is a well-known fact and was furthermore verified in other experiments not quoted here.

Acetic acid (or acetates) and citric acid did not give rise to contamination of the deposits. Other experimenters, however, have found results contrary to these, as was seen above. The discrepancy may be due to different experimental conditions, for instance, the acidity of the bath may be an important factor.

Carbon monoxide as well as carbon dioxide causes contamination of nickel deposits. The effect of these gases on iron was not studied.

Illuminating gas has only a negligible effect on the deposition of iron, while a large quantity of organic substance is introduced in nickel deposits. From Table I it will be seen that in the presence of illuminating gas, a ferrous ammonium sulfate electrolyte gives more carbonaceous matter in the deposited iron than does either a plain sulfate or chloride solution (Runs 12, 11, 16 and 22).

Acetylene is by far the most effective agent in giving rise to contamination of the deposits, both of iron and nickel.

Of special interest are the experiments in which a diaphragm

Table II.

Deposition of Nickel in the Presence of Organic Matter.

The experimental conditions are described on page 91.

No.	Composition of Electrolyte g./L.	Current Density amp./dm.^{2}	Time hr.	Metal Deposited g.	Type of Residue
39	120 g. nickel sulfate. 20 g. amm. chloride. 40. g. boric acid. Free acetic acid.	0.5	18	0.147	No residue.
40	120 g. nickel sulfate. 20 g. amm. chloride. 40 g. boric acid. Nickel acetate.	0.5	3	0.712	No residue.
59	120 g. nickel sulfate. 20 g. amm. chloride. Citric acid.	0.75	3	0.024	No residue.
31	120 g. nickel sulfate. 20 g. amm. chloride. 40 g. boric acid. Illuminating gas.	0.5	4	1.16	Strongly adherent film of brownish color left on the cathode after dissolving the metal.
26	120 g. nickel chloride. 20 g. amm. chloride. 40 g. boric acid. Acetylene.	0.5	6	About 1.5	Small amount of organic matter.
32	120 g. nickel sulfate. 20 g. amm. chloride. 40 g. boric acid. Diaphragm around anode. Acetylene in cathode compartment.	0.5	10	1.40	Thick, brown colored film left on the cathode.
58	120 g. nickel sulfate. 20 g. amm. chloride. 40 g. boric acid. 40 cc. 3% H_2O_2. Acetylene.	0.75	3	0.074	Film of black, flaky organic matter.
37	120 g. nickel sulfate. 20 g. amm. chloride. 40 g. boric acid. Carbon dioxide.	0.5	20	1.12	Film of organic matter.
38	120 g. nickel sulfate. 20 g. amm. chloride. 40 g. boric acid. Carbon dioxide.	0.5	18	0.77	0.0048 g. organic matter = 0.63% of total deposit.

TABLE II—*Continued.*

No.	Composition of Electrolyte g./L.	Current Density amp./dm.^{2}	Time hr.	Metal Deposited g.	Type of Residue
41	120 g. nickel sulfate. 20 g. amm. chloride. 40 g. boric acid. Carbon monoxide.	0.5	3	0.308	Small quantity of organic matter.
55	120 g. nickel sulfate. 20 g. amm. chloride. 40 g. boric acid. Diaphragm around anode. Carbon monoxide in cathode compartment.	1.0	8	0.247	Small quantity of organic matter.

(porous cup) separated the anode and cathode compartments. If the contamination of the deposits really was due to co-precipitation of colloids formed by alternating cathodic reduction and anodic oxidation, as called for by Foerster's theory, then it would certainly be expected that the introduction of a diaphragm would decrease the amount of organic matter deposited, since the porous medium would offer a great resistance to the transference of colloidal substances. No such effect was observed. In the case of nickel deposition a diaphragm did not exert any visible effect on the quantity of organic impurities caused by acetylene or carbon monoxide. In the two experiments, No. 13 and 20, Table I, quantitative determinations of the residues were made (drying of the organic matter at 105° C.). It will be seen that the percentage residue calculated on the deposited iron is approximately halved when the anode is surrounded by a diaphragm. However, it should be remembered also that another effect of the diaphragm is to increase the yield of deposited iron, since it partly prevents the acid liberated at the inert anode from diffusing over to the cathode. Thus, the yield of carbonaceous matter, if calculated on the total current passed through the two cells, is slightly higher with a diaphragm than it is without, a result which indicates that anode reactions can hardly play an important role in building up the impurities found in the cathode in this specific case. Additional data are given in Table III showing the same result, namely,

that the actual yield of carbonaceous matter is highest when a diaphragm is applied.

In experiment No. 58, Table II, hydrogen peroxide was added to the nickel sulfate electrolyte in view of the beneficial effect observed by Madsen, when applying this agent in nickel plating baths. No improvement was obtained in this case, however, where acetylene was bubbled into the solution.

TABLE III.

Effect of Acetylene on Electro Deposition of Iron.

Electrolyte, 300 cc. of a solution of 535 g./L. ferrous chloride. Cathode, platinum foil, 0.35 dm.^{2} Cathodic current density, 2 amp./dm.^{2} Anode, platinum wire. Temperature, 25° C. Time, 3 hr.

	Without diaphragm	With diaphragm
Deposited	1.744 g.	2.122 g.
Current efficiency	75 per cent	90 per cent
Residue	0.0136 g.	0.0222 g.
Combustible matter in residue	0.0132 g.	0.0141 g.
Combustible residue calculated on total deposit	0.76 per cent	0.67 per cent

2. *Deposition of Iron Using Anodes Containing Carbon.*

In the electrodeposition of iron on a commercial scale the carbon present in the iron anodes gives rise to contamination of the metal deposited at the cathode. According to Foerster (*l. c.*), this is due to anodic oxidation, causing the formation of organic colloids, which in turn are deposited together with the metal at the cathode. In order to study the possible formation of such colloidal materials, the two experiments quoted in Table IV were performed, using impure iron anodes at different current densities. The conditions were entirely the same in the two runs except that the size of the anodes was varied, so as to give an anodic current density of 4.0 and 0.5 amp./sq. dm., respectively.

No visible residue was detected in either of the deposits. However, if there really were a tendency for colloidal substances to

form at the anode, such products ought to be present in the electrolyte at the end of the run, considering that a current of about 0.25 amp. was passed through for 8 hours. With this in view, the volume of the electrolytes had been reduced to the smallest possible quantity, 150 cc., in order to facilitate the detection of any colloids by the ordinary methods used for such purpose.

TABLE IV.

Iron Anodes Containing Carbon.

Electrolyte, 150 cc. of a solution of 535 g./L. ferrous chloride. Temperature, 25° C. Time, about 8 hr.

	I	II
Cathode	Platinum foil 0.1275 dm.^{2}	Platinum foil 0.1275 dm.^{2}
Anode	Iron wire 0.0625 dm.^{2}	Iron wire 0.50 dm.^{2}
Cathodic C. D.	2.0 amp./dm.^{2}	2.0 amp./dm.^{2}
Anodic C. D.	4.0 amp./dm.^{2}	0.5 amp./dm.^{2}
Deposited at the cathode	2.021 g.	2.025 g.
Dissolved at the anode	2.496 g.	2.310 g.
Organic residue in deposit	None	None

The change in viscosity during the run could not be used as a basis for definite conclusions as to the colloidal character of the solutions, since evaporation from the surface of the electrolytes could not be avoided. That no appreciable amount of colloids had been formed, however, was proved by the fact that the surface tension of the solutions remained unchanged. The surface tension, which is usually a very delicate test for colloidal matter, was measured with a Donnan pipette, giving a constant drop weight of 0.03728 g. before and after the passage of the current in both runs.

Furthermore, the two electrolytes were examined under the ultramicroscope. In order to avoid the disturbing influence of ferric hydroxide formed during electrolysis, the solutions had to

be slightly acidified with hydrochloric acid. The solutions thus prepared were as optically clear as distilled water, and disclosed the same number of particles as the original solution when viewed under the ultramicroscope.

TABLE V.

Polarization of Iron Deposits in Electrolytes Containing Organic Matter.

The experimental conditions are described on page 97.

No.	Started with deposit of:	Polarization Period			Type of Residue
		Electrolyte g./L.	Current Density amp./dm.^{2}	Time hr.	
7	7.42 g. iron deposited from chloride electrolyte.	50. g. ammonium oxalate	2.0	48	Finely divided black substance.
8	3.53 g. from sulfate electrolyte.	50. g. ammonium oxalate	2.0	32	As in No. 7.
9	9.16 g. from chloride electrolyte.	50. g. ammonium oxalate	2.0	42	As in No. 7 and 8, but less.
14	4.34 g. from sulfate electrolyte.	50 g. amm. carbonate, acetylene	2.0	20	Black substance left upon dissolution of metal.
15	1.86 g. from sulfate electrolyte.	50 g. amm. carbonate	2.0	20	Black residue, about ⅕ of the one in No. 14.*
17	2.17 g. from chloride electrolyte.	50 g. amm. oxalate, illuminating gas	2.0	20	0.0022 g. organic substance.†
18	2.24 g. from chloride electrolyte.	50 g. amm. oxalate	6.0	20	Negligible compared with No. 7 and 9.
21 b	1.79 g. from chloride electrolyte.	50 g. amm. carbonate	2.0	60	About 20 mg. organic matter.
21 a	2.07 g. from chloride electrolyte.	50 g. amm. oxalate	2.0	60	About 5 mg. Compare No. 21 b.

* Acetylene was not present in this run.

† More than without illuminating gas in No. 7, 8 and 9.

TABLE VI.

Polarization of Nickel Deposits in Electrolytes Containing Organic Matter.

The experimental conditions are described on this page.

No.	Started with deposit of:	Polarization Period			Type of Residue
		Electrolyte g./L.	Current Density amp./dm.^{2}	Time hr.	
27 a	1.11 g. nickel deposited from sulfate electrolyte.	50 g. ammonium oxalate	2.0	20	None.
27 b	1.20 g. from sulfate electrolyte.	50 g. ammonium carbonate	2.0	20	None.
28	0.25 g. from complex ammonia electrolyte.	17 g. amm. sulfate, free ammonia, acetylene	1.5	18	Thick brown film covering the platinum cathode after dissolving the metal.
29	0.25 g. from complex ammonia electrolyte.	17 g. amm. sulfate, free ammonia, illuminating gas	1.5	18	A very thin film left on the cathode, lighter in color than the one in No. 28.
47	1.13 g. from sulfate electrolyte.	33 g. amm. oxalate	3.0	9	None.
48	1.17 g. from sulfate electrolyte.	33 g. amm. carbonate	3.0	9	None.

3. *Polarization of Iron and Nickel in Solutions Containing Organic Matter.*

The previous experiments on electrodeposition in the presence of organic matter having failed to show any indication of a co-precipitation of colloidal substance at the cathode, a series of runs were made in which pure iron and nickel were polarized cathodically in electrolytes containing the same kind of organic substances as were used before. The results of these experiments are given in Tables V and VI. The metal in question was first deposited electrolytically on platinum foil, 0.35 sq. dm. in area, from a solution of one of its chemically pure salts in distilled

water (second column in both tables), and was afterwards polarized under the conditions stated in the tables. The anodes consisted of platinum wires. When gases were used, these were bubbled into the electrolyte from the bottom. The temperature was kept between 25° and 28° C. The last column refers to the observations made when dissolving the deposits according to Classen's method.

Summary of Results. Ammonium oxalate causes contamination of iron, but not of nickel. The same holds true for ammonium carbonate. Ammonium carbonate is more effective than the oxalate in contaminating iron.

Carbonaceous matter is introduced in both iron and nickel, when these metals are polarized in solutions into which illuminating gas or acetylene is bubbled.

The nickel deposits, initially smooth and dense of a greyish color, had a tendency to become black during the period of polarization, whether or not any carbonaceous matter was found upon dissolution of the metal. This is in accordance with an observation by Raoult,[19], namely, that nickel may be disintegrated to a fine powder when polarized cathodically in an acid solution. This phenomenon is probably due to the building-up and breaking-down of nickel hydride on the electrode surface.[20] The iron deposits were unchanged in their appearance after the polarization. No film of organic matter could be detected on the surface, either with the naked eye or with the microscope. Attempts were made in the case of iron to dissolve the outer layer first, and afterwards treat the remaining metal separately with the Classen solutions. In such cases nearly all of the residue would be found in the second solution, indicating that the carbonaceous matter was situated in the interior of the solid metal.

These observations can not be explained by the theory of co-precipitation of colloids.

4. *Experiments on Electro Analysis of Iron and Nickel Using Complex Oxalate Electrolytes.*

The quantitative deposition of iron and nickel from oxalate electrolytes has been the subject of extensive study. The results,

[19] Raoult, Compt. rend., **69**, 826.

[20] P. K. Frölich, Discussion of paper by Prof. Kohlschütter, Trans. Am. Electrochem. Soc., **45**, 240 (1924).

which will be published elsewhere may be briefly summarized as follows:

Nickel deposited from a complex oxalate electrolyte always contains carbonaceous matter to an extent of from 1 to 2.5 per cent, calculated on the theoretical yield of metal. It was impossible to reduce the excess weight of the deposit to less than about 1 per cent, although both temperature, cathodic current density, and anodic current density were varied within wide limits.

A porous cup used as a diaphragm did not cause the nickel to be deposited in a pure state, as reported by Lambris (*l. c.*). The same kind of residue was found in this case as when no diaphragm was used.

In view of Madsen's experience with hydrogen peroxide in nickel deposition, experiments were made with this substance added to the oxalate electrolyte. The results were negative.

Unlike nickel, iron is not contaminated in the beginning of the electrolysis. However, before the iron is completely deposited, carbonaceous matter appears in the metal. From then on the amount of impurities increases with the time, even after all the iron has been deposited. Thus, the electrolysis may be discontinued at a point where nearly quantitative deposition is secured, and only a slight contamination has taken place, but it is not possible to obtain 100 per cent deposition of absolutely pure metal from the ordinary oxalate electrolyte.

In the experiments reported in Table I, it was found that ammonium oxalate did not cause contamination of iron, when ferrous chloride was substituted for ferrous ammonium sulfate in preparing the electrolyte. Likewise, illuminating gas gave only a small residue in the case of a ferrous chloride electrolyte. Use was made of these observations in preparing an electrolyte, which would secure quantitative deposition of absolutely pure iron. It was found that an addition of ammonium chloride to the ordinary iron oxalate electrolyte would prevent any organic matter from contaminating the deposit, for a period more than sufficient for quantitative deposition of the metal, while sodium chloride did not have the same effect. On the other hand, ammonium chloride increased the percentage of residue found in nickel deposited from oxalate.

5. *Ultra-microscopic Examination of the Iron and Nickel Electrolytes.*

Samples of all the different types of electrolytes studied in the preceding experiments were examined under the ultramicroscope. It may be sufficient to state that the results were entirely negative, as regards any detection of colloids. In most cases the electrolytes contained the same number of particles at the end of the electrolysis as they did at the start, and possessed about the same colloidal character as that of ordinary distilled water.

6. *Character of Residues.*

The residues from the contaminated nickel always had a pronounced film structure, as may be seen from the accompanying photomicrographs. Upon dissolution of the nickel the platinum cathode was found to be covered with organic matter, which sometimes would stick firmly to the metal. Viewed under the microscope, the individual flakes appeared to be more or less transparent, depending on the quantity of residue, that is, on the thickness of the film. The transparent character is best seen from Fig. 3 and 5. The color varied from yellowish brown to dark brown or black. When the residues were treated with hydrochloric acid chlorine was liberated. On heating, the flakes would curl up and apparently decrease in volume. The residue would ignite at a fairly low temperature and burn completely. Thus there are strong indications that the carbon is present in the metal in the form of complex hydrocarbons. This is in accordance with the analyses by Lambris and others,[11] which showed that a certain percentage of hydrogen was present in nickel residues.

With iron the results were somewhat different. Thus, in some cases it appeared to be difficult to remove the iron quantitatively from the organic matter, although treatment with hydrochloric acid would secure ash-free residues. Fig. 6 shows one of the iron residues. The flaky structure is not so distinct as in the case of nickel. The tread-shaped particles are cellulose fibers which were introduced by filtration of the Classen solution.

DISCUSSION OF RESULTS.

Our present knowledge as to the possible products of electroreduction and oxidation of organic compounds of as simple a

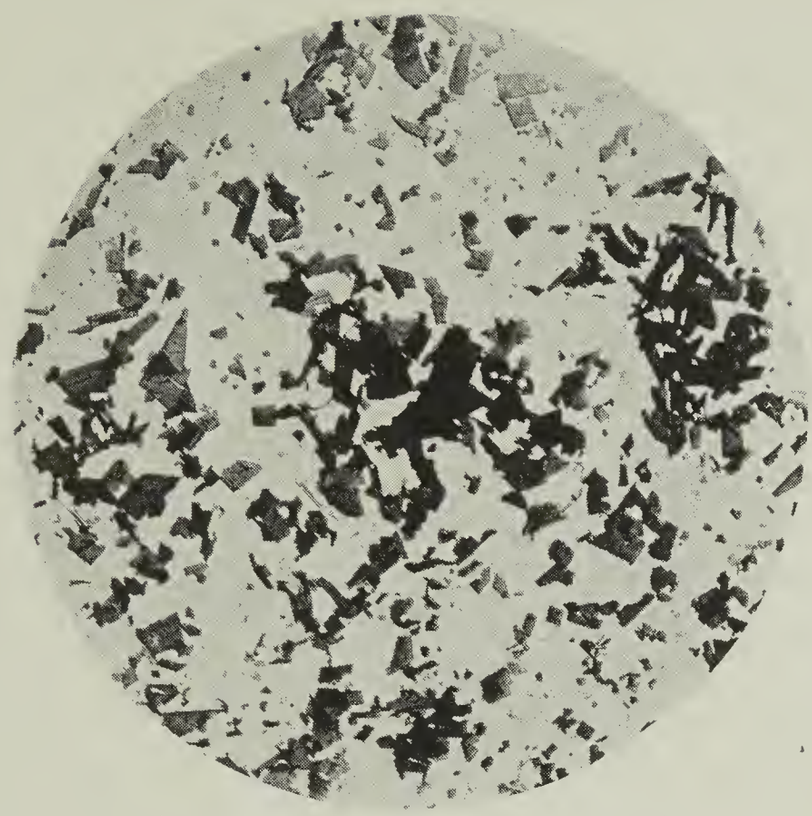


FIG. 1. x 25

Typical residue from nickel deposited from complex oxalate electrolytes. (No. 35.)

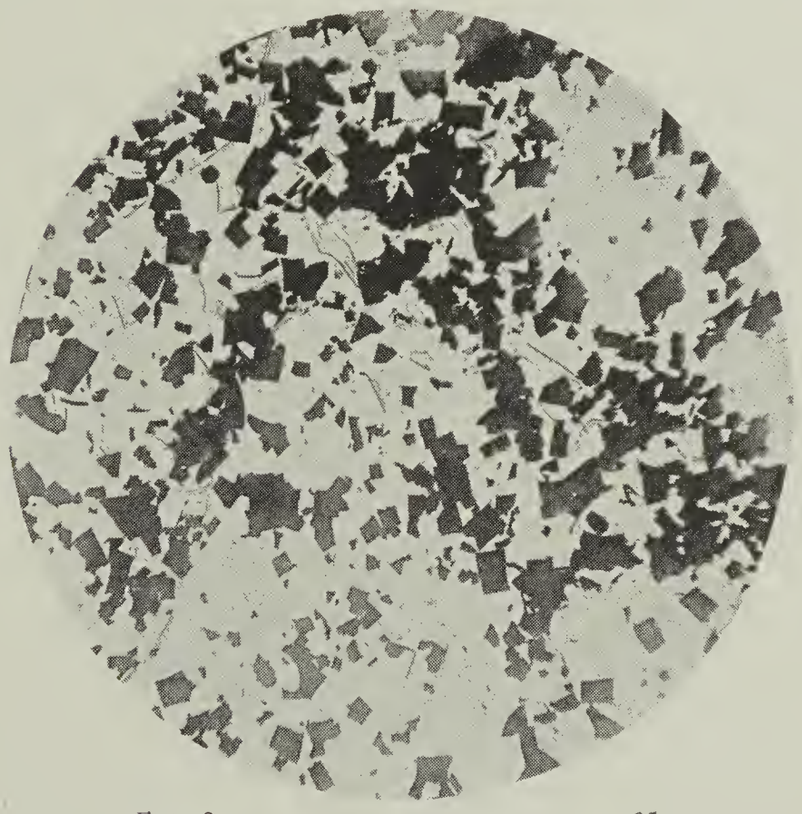


FIG. 2. x 25

Typical residue from nickel deposited from complex oxalate electrolytes. (No. 36.)

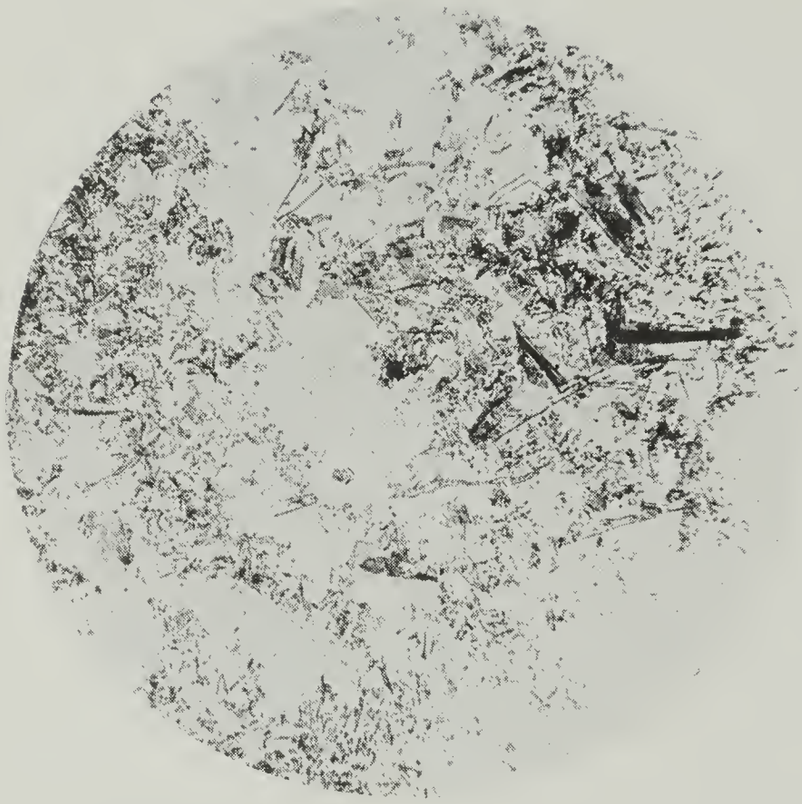


Fig. 3. x 25

Nickel sulfate electrolyte with carbon monoxide. Table II. (No. 55.)

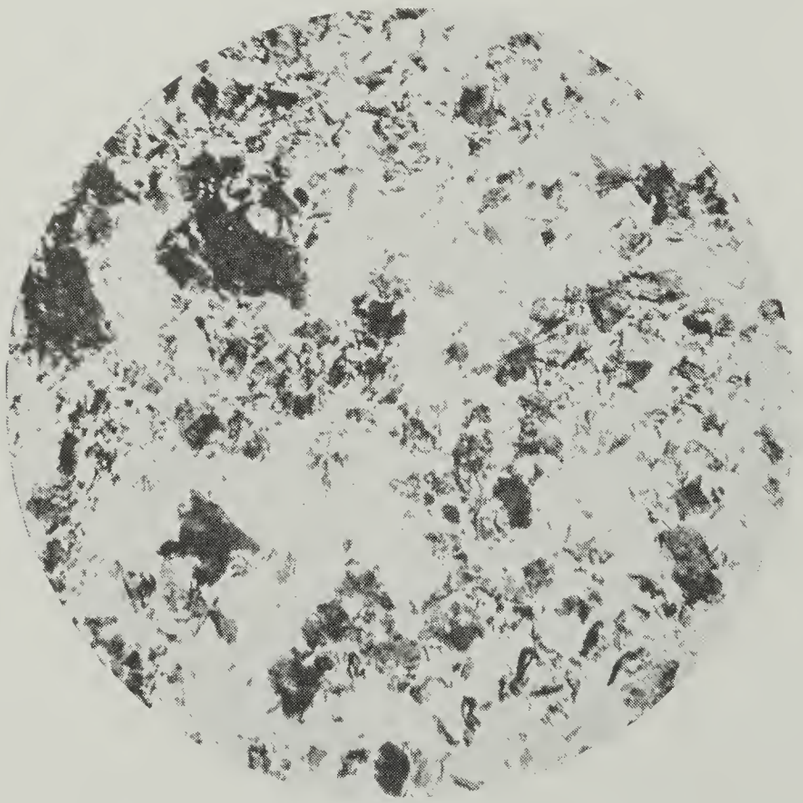


Fig. 4. x 22

Nickel sulfate electrolyte with acetylene. Table II. (No. 32.)

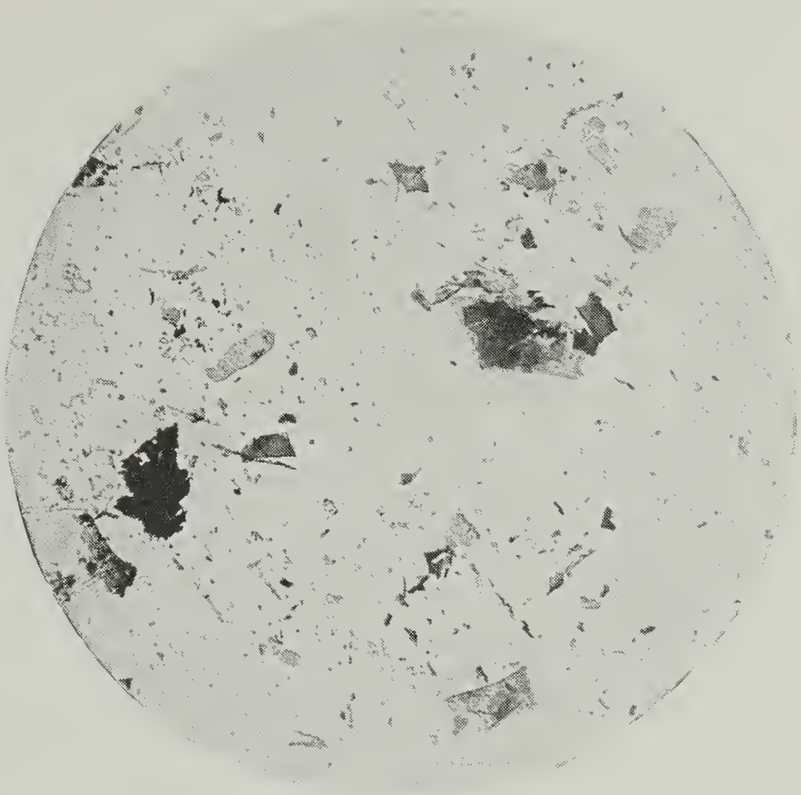


Fig. 5. x 25

Nickel sulfate electrolyte with illuminating gas. Table II. (No. 31.)

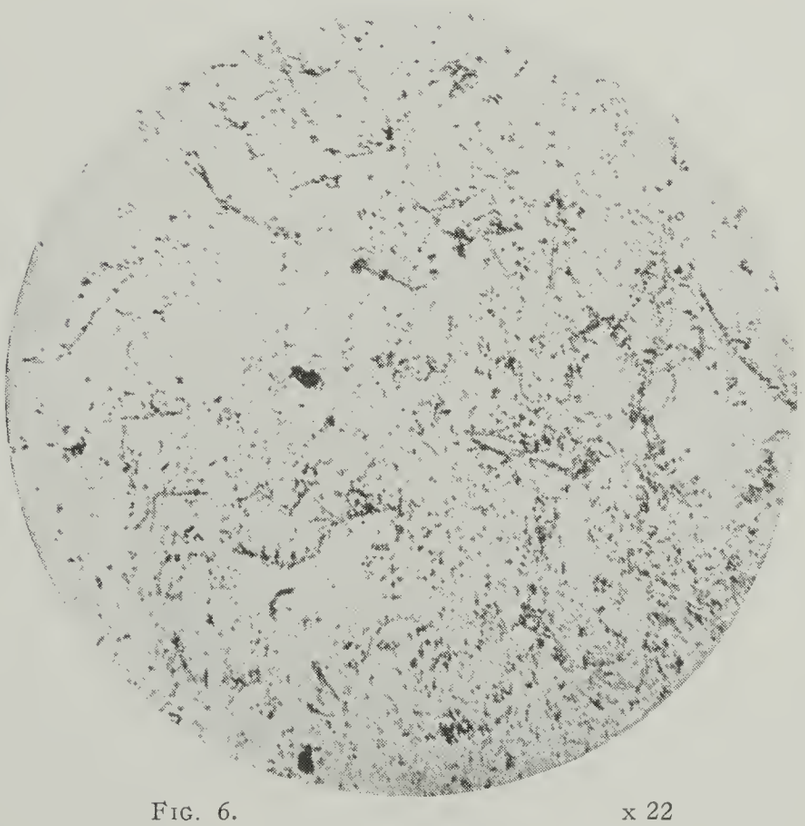


Fig. 6. x 22

Residue from iron deposited from a complex oxalate electrolyte. (No. 68.)

composition as oxalic acid, the oxides of carbon, and acetylene makes it difficult to draw conclusions regarding the mechanism of the phenomena in question. However, it may be said that the explanation offered by Avery and Dales, demanding a cathodic reduction of the organic material down to elementary carbon, is hardly tenable in view of other observations in organic electro chemistry in general.

Furthermore, the characteristics of the residues as disclosed by this work prove that the carbon is not present in the elementary state (at least, not in the case of nickel). Thus, it was mentioned above that the residues had a film structure, that these films were more or less transparent, and also seemed to possess a certain oxidizing power, since chlorine would be liberated when the organic matter was treated with hydrochloric acid.

Foerster's theory of alternating cathodic reduction and anodic oxidation, followed by electro-osmotic transference and precipitation at the cathode of the colloids thereby formed, fails to account for a number of the present observations. Thus it was seen that a diaphragm between the anode and cathode did not slow down the processes leading to contamination of the metal deposited at the cathode. Carbonaceous matter was found in pure metals, after polarization in electrolytes containing nothing but a conductivity salt and some kind of an organic substance. It was also shown that the impurities in these cases were situated in the interior of the metal, and did not consist merely of a surface coating. No colloidal matter could be detected in any of the electrolytes, either by surface tension measurements or by the ultramicroscope. All these facts, as well as the observation by Skrabal that the organic impurities liberated by anodic dissolution of oxalate-iron will not be deposited again at the cathode, are in apparent opposition to the theory of a co-precipitation of colloid and metal.

Lambris suggested that the organic impurities were formed in the cathode, owing to the catalytic activity of nickel or iron with respect to reactions leading to decomposition of acetylene formed by cathodic reduction. Also the results of the present investigation indicate catalytic reactions with the cathode metal as the active catalyst, a view which seems to be supported by all the observations made. The decomposition of the gases, however,

apparently does not lead to formation of carbides or elementary carbon, as was assumed by Lambris. (Compare the above observations as to the nature of the residues.)

Other facts which point towards the catalytic conception are that, in addition to iron and nickel, cobalt also contains carbonaceous matter when deposited from an oxalate electrolyte, while zinc, cadmium, and tin do not.[21] Nickel, but not zinc, contains sulfur, when deposited from a hot ammoniacal electrolyte containing sulfite, and iron from commercial electrolytes contains sulfur and phosphorus, in addition to carbon monoxide and solid carbonaceous matter. From this it will be seen that the metals which give rise to contamination are especially the metals of the iron group, all of which are known to be positive catalysts in numerous gas reactions. It may also be possible that the hydrogen content of these metals, when polarized cathodically, is of importance. The arbitrary choice of the experimental conditions, however, does not permit of any final conclusion as to the mechanism of the reactions leading to contamination of the deposits. Further research will be required to disclose the exact nature of the phenomenon.

The scope of this work was to investigate the colloidal part of the problem, and in this respect the results are conclusive in that they show that a co-precipitation of colloidal matter does not take place *under the conditions studied.* This conclusion is further evidence of the fact that too frequently recourse is taken in the literature to "colloidal action" and similar terms, as an explanation of various phenomena, without adequate experimental basis.

CONCLUSIONS.

1. Organic gases or salts present in the electrolyte may cause contamination of electrodeposited metals of the iron group.

2. Polarization of iron and nickel in solutions containing organic matter may cause contamination of the metal. The organic impurities thus introduced are situated in the interior of the solid metal.

3. Co-precipitation of colloids does not cause the contamination under the conditions studied. The organic impurities are prob-

[21] Experiments by the writer confirmed these results for zinc.

ably products of gas reactions, catalyzed by the deposited metal, and do not consist of elementary carbon. A closer study of the cathode processes is desirable.

4. In the case of iron and nickel deposition from complex oxalate electrolytes, the processes leading to contamination of the metal are more or less affected by the inorganic ions present in the bath.

Thanks are due to V. O. Homerberg and Miss F. H. Clark for preparation of the photomicrographs and to Dr. G. L. Clark for assistance in reviewing the paper.

DISCUSSION.

W. Blum[22]: The paper is of decided interest, because the results are not the sort you would predict or anticipate. The author has indicated that the paper is distinctly preliminary, and, therefore, it should not be construed in any sense as a criticism to point out some of the limitations in his experimental conditions, that is, the factors which should be controlled in a more detailed research. In general, it is desirable to use the normalities or equivalents in expressing the concentration of the solutions, which makes it easier to draw valid comparisons. The control of acidity has an important effect on the deposition of the iron and nickel, and probably also on the co-precipitation of the organic materials to which Dr. Frölich refers. In any future study the potential relations should be considered. Dr. Frölich states that organic matter is deposited with the iron from a ferrous ammonium sulfate solution in the presence of an oxalate, but not from a ferrous chloride solution. It can be shown, I think, with certainty that the iron from a ferrous chloride solution is deposited at a lower (less negative) potential than from a ferrous ammonium sulfate solution. If then, a certain potential is required for the electrolytic action which brings about the inclusion of organic matter, that potential may be reached in a ferrous ammonium sulfate solution, but not in a ferrous chloride solution. If ammonium

[22] Chemist, Bureau of Standards, Washington, D. C.

chloride is added to the former solution, it may bring about the same potential relations as would exist in a solution which originally contained ferrous chloride.

F. C. MATHERS[23]: Why is it necessary to assume that the organic matter found in the cathode is the result of catalytic decomposition? A soluble salt or a metal that normally does not deposit may be deposited with a metal on the cathode. I feel that a complex cation, made up of all the substances in the bath, may be deposited. In Dr. Frölich's experiments such a complex in the cathode was decomposed by the copper sulfate, with the formation of the carbon flakes. As much as one per cent of iron as well as the tartrate radical can be deposited with silver from a bath of silver nitrate, ferric nitrate, nitric acid and tartaric acid. The fact that hydrochloric acid prevented the formation of the carbon flakes in the cathodes agrees with the experimental fact that even small quantities of hydrochloric acid prevent various addition agents from giving smooth deposits of metal.

PER K. FRÖLICH: I agree entirely with Dr. Blum that electrode potential determinations should not be overlooked in a study of the nature of the reactions responsible for the contamination. The importance of the electrode potentials becomes apparent when it is considered that the gases, which are supposed to undergo decomposition at the cathode, have to be formed by electrolytic reduction (oxidation). I hope some one will take up the study of this part of the problem. We were interested primarily in the colloidal aspect of it.

My experiments were started originally in connection with our study of addition agents. Thus it has already been shown[24] that the results obtained are helpful in explaining the apparently abnormal behavior of nickel, relative to zinc, when these metals are deposited in the presence of gelatine.

I do not quite see how a complex ion included in the deposit, as assumed by Dr. Mathers, could result in the formation of residues such as those disclosed in the photomicrographs. No reduction or breaking down of the organic substance seems possible when copper chloride solution is used as a solvent.

Furthermore, the theory of the complex ion does not explain

[23] Prof. of Chemistry, Univ. of Indiana, Bloomington, Ind.
[24] This volume, page 67.

the polarization experiments quoted in this paper. Neither do I think it can account for the effect of minute traces of organic matter used as addition agents in electrodeposition. Also the wide use of complex salts in electroanalysis, where the highest purity of the deposit is sought, is against the conception of cathodic deposition of the complex ion as such. In this connection it would be interesting to know if Dr. Mathers found any stoichiometric relation between the ion and the organic substance in his deposit.

F. C. MATHERS: The test for the organic matter was the unmistakable odor of decomposing tartaric acid, when the silver cathodes were ignited.

A paper presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 3, 1924, President Parmelee in the Chair.

THROWING POWER, CATHODE POTENTIALS AND EFFICIENCIES IN NICKEL DEPOSITION.[1]

By H. E. Haring.[2]

Abstract.

The throwing power of nickel solutions was determined by means of the apparatus previously described. The cathode potentials and efficiencies during nickel deposition were measured. The results show that the chief factor in throwing power in nickel deposition is the cathode efficiency. This is determined principally by the ratio of the effective nickel and hydrogen ion concentrations in the cathode film. All conditions which increase this ratio improve throwing power.

I. INTRODUCTION.

In electroplating it is desirable, but difficult, to obtain a nearly uniform deposit of metal upon the surface of the article plated. Solutions from which the most nearly uniform metal distribution is secured are said to possess good "throwing power." In a previous publication[3] this property was defined and measured, and the underlying principles were illustrated with copper sulfate and cyanide solutions.

In connection with a general study of nickel deposition in progress at the Bureau of Standards, the throwing power of nickel solutions was determined under definite conditions. These measurements included interesting observations upon the cathode potentials and efficiencies during nickel deposition.

[1] Manuscript received July 14, 1924. Published by permission of the Director, Bureau of Standards, Department of Commerce, Washington, D. C.

[2] Associate Chemist, Bureau of Standards, Washington, D. C.

[3] "Current Distribution and Throwing Power in Electrodeposition," H. E. Haring and W. Blum. Trans. Am. Electrochem. Soc., 44, 313 (1923).

II. HISTORICAL.

In the paper by Haring and Blum,[4] reference is made to previous publications upon throwing power. The only important paper published since that time is by A. H. Heatley,[5] who presented a mathematical derivation of the current relations in multiple electrode systems. From such calculations Heatley showed that the equations used in the paper by Haring and Blum were not general, although they represented the conditions in the apparatus employed by these authors. It was shown that the ratio of the "effective resistances" to two parts of a cathode lying upon the same side of the anode is not constant, but changes with the current passing to these points. In other words, the current passing to one part of a cathode has an influence on the current passing to another part of the cathode, and a readjustment of the current distribution follows. This effect is due to the fact that the current tends to be distributed throughout the entire electrolyte. In view of the omission of any consideration of this factor in the paper by Haring and Blum, the objection has been raised that the results obtained with the "throwing power box" do not represent actual plating conditions.

The effect of such a factor even if it becomes appreciable, must be considered as a secondary one, similar to, for example, the effect of "pocketing" of solution in recesses, or variations in convection on the cathode surface, or local temperature differences.

Quantitative consideration of all these factors is an obvious impossibility. The "throwing power box" is merely a concrete representation of the most simple clearly defined case of throwing power imaginable. It isolates the fundamental factors and makes their quantitative measurement possible. Any results obtained in commercial practice will *parallel* those found with the "throwing power box," although they will undoubtedly be modified by intangible secondary factors.

III. GENERAL PRINCIPLES.

In the paper by Haring and Blum the fundamental principles of throwing power have been explained and illustrated. How-

[4] *Loc. cit.*

[5] "Multiple Electrode Systems," A. H. Heatley. Trans. Am. Electrochem. Soc., 44, 283 (1923).

ever, a brief review is desirable with special reference to nickel deposition.

"Throwing power" is there defined as "the deviation (in per cent) of the metal distribution ratio from the primary current distribution ratio" (that is, the current distribution when there is no polarization).[6] If, for example, the effective resistances from the anode to two parts of the cathode are in the ratio of 1 : 5, the primary current ratio is 5 : 1. If in such a case the metal distribution ratio on these two parts is 4 : 1, the throwing power is 20 per cent. Throwing power as thus defined has been shown, both mathematically and experimentally, to be dependent upon (a) the rate of change of cathode potential with current density, (b) the resistivity of the solution, and (c) the cathode efficiency at different current densities.

In the experiments on acid copper sulfate solutions described in the previous paper, the cathode efficiencies of copper deposition were practically 100 per cent, consequently factor (c), the cathode efficiency, was automatically eliminated. However, when the cathode efficiency changes with current density, it has an important effect on throwing power.

Cathode efficiency may either increase or decrease with increasing current density. The cathode efficiency is a measure of the relative tendencies of the metal and of hydrogen to be discharged under the prevailing conditions. These respective tendencies depend upon (a) the equilibrium potentials of the metal and hydrogen in the solution, (b) the "effective" concentrations of metal ions and hydrogen ions in the cathode film, and (c) the overvoltage of hydrogen discharge upon the metal.

As the current density is increased, the ions most easily discharged are depleted in the cathode film, and a higher potential is required for their continued discharge. Consequently the potential required for the discharge of the other ion is reached or passed; in other words, the tendencies toward discharge of the two ions become more nearly equal. With increased current density the ratio of ions discharged must approach as a limit the ion concentration ratio in the solution.

[6] Heatley (*loc. cit.*) proposes to define throwing power in terms of the maximum possible deviation. As, however, any such definition is arbitrary, and as in all cases the primary ratio must also be stated (or implied) it seems preferable to adhere to the slightly less complicated definition of Haring and Blum.

If in a given solution the static potential of the metal (for example, copper in a copper sulfate solution) is more positive (more noble) than that of hydrogen in that solution, the cathode efficiency will be practically 100 per cent at all current densities corresponding to potentials more positive than the static potential of hydrogen. Beyond that point the efficiency will *decrease* as the current density is increased. (Class 1.)

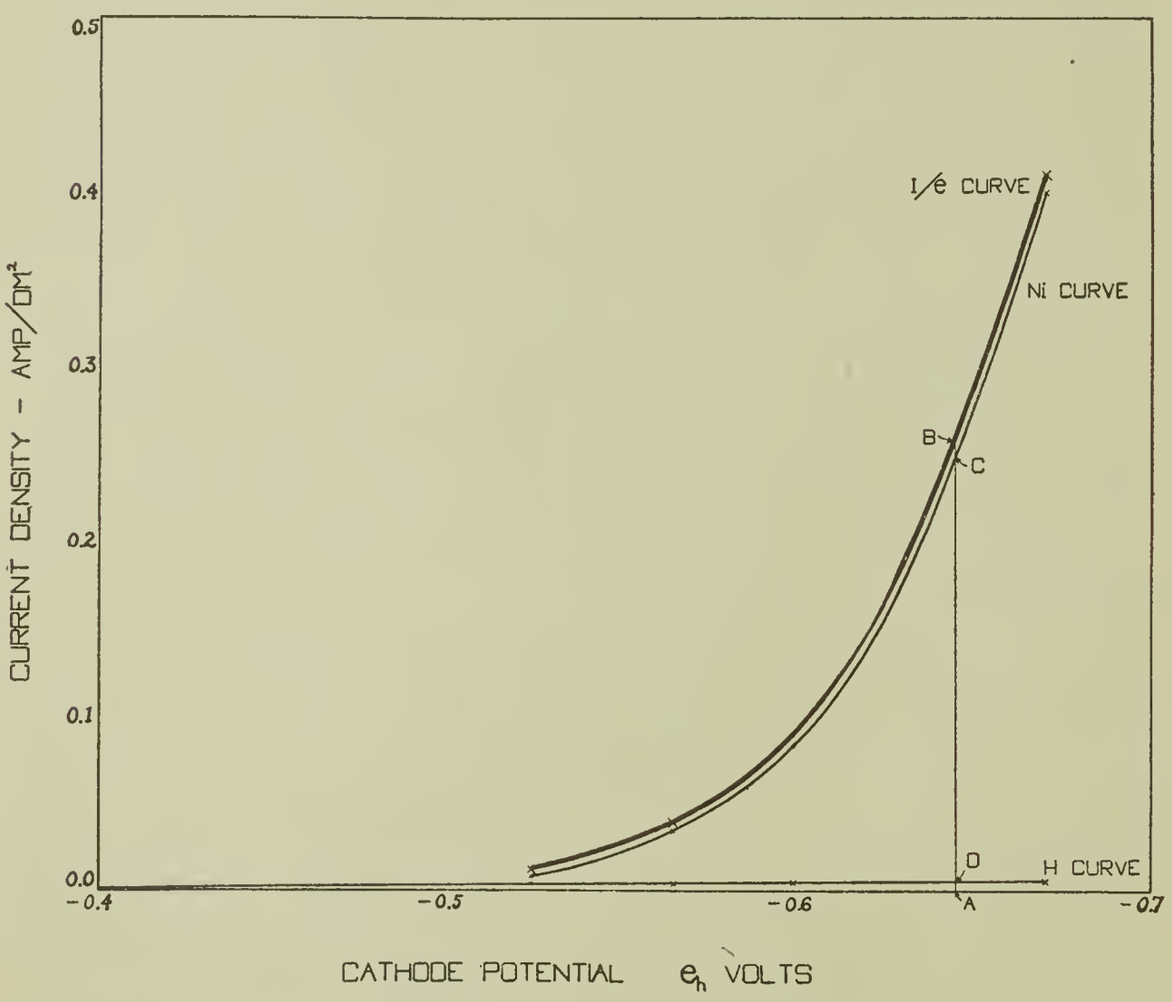


FIG. 1.
Graphic Analysis of Typical Current Density-Cathode Potential Curve in Nickel Deposition.

If in a given solution the static potential of the metal is more negative (less noble) than that of hydrogen, the conditions are reversed. At any potential, and corresponding current density, up to the static potential of the metal in that solution, hydrogen only will be discharged, and the metal cathode efficiency will be zero. If the current density is increased so that the potential is equal to or more negative than the static potential of the metal, the latter will be deposited, together with hydrogen, and the

cathode efficiency will *increase* as the current density is increased, but it can never actually reach 100 per cent. (Class 2.)

The relation of cathode potentials and efficiencies in the latter case is illustrated by Fig. 1, which represents a typical example of the conditions existing in nickel deposition.[7] The I/e (current density-cathode potential) curve is obtained by plotting the experimentally obtained cathode potentials against the current densities involved. The nickel curve and the hydrogen curve represent the cathode potentials plotted against the portions of the current used respectively for nickel and hydrogen discharge, as computed from the experimentally determined cathode efficiencies. The sum of the ordinates to these two curves at any given potential is equal to the ordinate to the I/e curve at that potential. For example, AC + AD = AB. The nickel cathode efficiency in per cent is then AC/AB × 100. It follows that the measurement of a discharge potential under any given conditions, for which these curves are already known, is also a measurement of the cathode efficiency.

This important relation between cathode potential, current density and cathode efficiency has been emphasized because, as will be shown, the cathode efficiency is the predominating factor in the throwing power of nickel solutions.

IV. MATERIALS AND METHODS USED.

In order to determine the effects of the principal operating variables, a "standard" solution was tested under appropriate conditions. The effects of changes in the composition of the solution were determined by means of the solutions listed in Table I. The acidity of all of the solutions at the beginning of an experiment was pH 5.7 to bromcresol purple, unless otherwise stated.

The apparatus and methods of operation were the same as described by Haring and Blum in the previous publication. The "throwing power box," as illustrated in Fig. 2, is used for the empirical determination of throwing power. Such a determina-

[7] As will be pointed out later, a consideration of the relative static potentials of nickel and hydrogen in a nickel plating bath would place such a bath in the first class, that is, with the acid copper sulfate solution. However, *in behavior,* the nickel bath belongs in Class 2, and hence it will be discussed from that viewpoint.

TABLE I.

Composition of Solutions Used.

To Determine Effect of	Solution	Constituents in Addition to H_3BO_3—0.25 M	Concentration			Resistivity* Ohm—cm. 21° C. (70° F.)
			N	g./L.	oz./gal.	
Nickel concentration.	A†	$NiSO_4.7H_2O$	1.0	140	19	21
		NH_4Cl	0.25	13	1.7	..
	B	$NiSO_4.7H_2O$	0.5	70	9.5	26
		NH_4Cl	0.25	13	1.7	..
	C	$NiSO_4.7H_2O$	2.0	281	38	18
		NH_4Cl	0.25	13	1.7	..
Substitutions for NH_4Cl	D	$NiSO_4.7H_2O$	1.0	140	19	23
		NaCl	0.25	15	2	..
	E	$NiSO_4.7H_2O$	0.75	105	14	28
		$NiCl_2.6H_2O$	0.25	30	4	..
	F	$NiSO_4.7H_2O$	1.0	140	19	23
		$MgCl_2.6H_2O$	0.25	25	3.3	..
	G	$NiSO_4.7H_2O$	1.0	140	19	37
		No chloride				
	H	$NiSO_4.7H_2O$	1.0	140	19	24
		$(NH_4)_2SO_4$	0.25	17	2.3	..
	I	$NiSO_4.7H_2O$	1.0	140	19	27
		NaF	0.25	11	1.5	..
'All chloride' solutions..	J	$NiCl_2.6H_2O$	1.0	119	16	15
	K	$NiCl_2.6H_2O$	1.0	119	16	12
		NH_4Cl	0.25	13	1.7	..
Additions...	L	A + $Na_3C_6H_5O_7.5.5H_2O$ (citrate)	0.5	60	8.0	17
	M	A + Dextrin	. . .	5	0.7	21
	N	A + H_2O_2		10‡	1.3‡	21
	O	A + Na_2SO_3	0.015	1	0.13	21
Impurities ..	P	A + $CdCl_2.2H_2O$	0.001	0.11	0.015	21
	Q	A + $CuSO_4.5H_2O$	0.001	0.13	0.017	21
	R	A + $ZnSO_4.7H_2O$	0.001	0.14	0.019	21

* Approximate values computed from the data of the throwing power experiments.
† "Standard."
‡ 10 cc./L. or 1.3 fl. oz./gal. of 3 per cent H_2O_2 solution.

tion involves only the gain in weight of the two cathodes. The throwing power in per cent is expressed by the equation:

$$T = \frac{K - \frac{M_n}{M_f}}{K} \times 100$$

in which T is the throwing power in per cent, M_n and M_f are the weights of the deposit upon the near and far cathodes respectively, and K is the primary current distribution ratio, that is, the inverse ratio of the resistances to the two parts of the cathode. K = 5 for the data given in this and the previous paper.

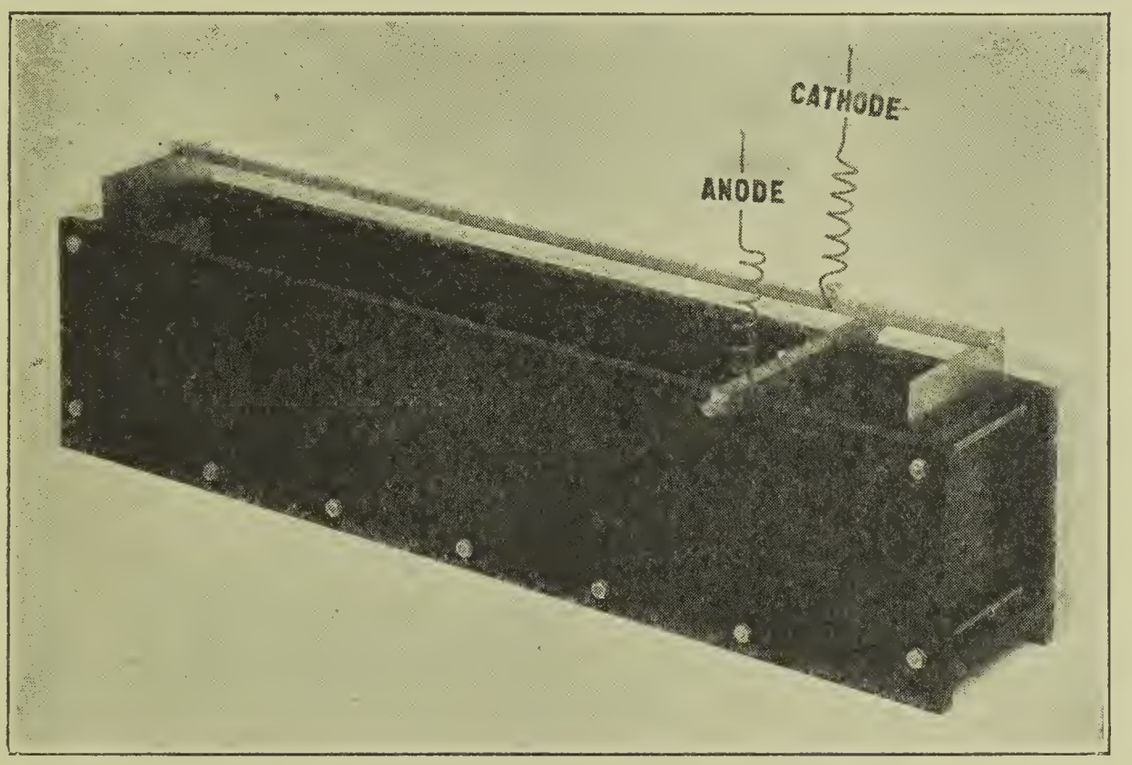


Fig. 2.
The "Throwing Power Box."

As in the earlier paper, the results computed from the weights of the deposits were confirmed by calculations from the potentials involved. In all cases the agreement was within the limit of error of the experiments, that is, within two per cent of the values. This agreement is a further proof that throwing power is the resultant of the three previously mentioned factors.

It was not found practicable to obtain pure nickel gauze, consequently a perforated platinum sheet heavily plated with pure

Table II.

Throwing Power in Nickel Solutions.

"Standard Conditions"* Primary Ratio 5:1; $NiSO_4$-*N*; NH_4Cl-0.25 *N*; H_3BO_3-0.25 M; pH-5.7; Temperature 21° C. (70° F.)

Effect of	Solution	Total Current Amp.	Current Ratio Obtained	Efficiency Per cent "n"	Efficiency Per cent "f"	Metal Ratio Obtained	Throwing Power Per cent
Current density....	A	0.05*	3.22	86	67	4.18	16.4
	A	0.25	4.38	95	84	4.96	0.8
	A	0.50*	4.61	98	91	4.92	1.6
	A	1.00	4.71	98	92	5.00	0.0
	A	1.50	4.84	99	95	5.04	—0.8
Temperature 45° C.	A	0.05	3.41	78	49	5.47	—9.4
	A	0.50	4.48	97	90	4.88	2.4
Agitation:							
Air	A	0.05	2.93	56	16	10.21	—104.2
	A	0.50	4.62	94	75	5.78	—15.6
Mechanical (uniform)....	A	0.05	3.14	71	26	8.56	—71.2
	A	0.50	4.66	95	74	6.00	—20.0
Mechanical (local).....	A	0.05	3.14	65	73	2.81	43.8
	A	0.50	4.63	96	92	4.80	4.0
Acidity and nickel concentration:							
pH 4.5.....	A	0.05	3.18	85	62	4.38	12.4
	A	0.50	4.63	97	91	4.97	0.6
pH 6.5.....	A	0.05	3.35	89	73	4.10	18.0
	A	0.50	4.62	98	95	4.76	4.8
0.5 *N* Ni.....	B	0.05	3.48	86	64	4.69	6.2
	B	0.50	4.68	97	91	5.01	—0.2
2.0 *N* Ni.....	C	0.05	3.21	89	73	3.90	22.0
	C	0.50	4.57	98	93	4.79	4.2
Substitutions for NH_4Cl:							
NaCl	D	0.05	3.31	87	68	4.28	14.4
	D	0.50	4.62	97	90	4.94	1.2
$NiCl_2$	E	0.05	3.71	90	75	4.45	11.0
	E	0.50	4.68	98	93	4.93	1.4
$MgCl_2$	F	0.05	3.47	88	70	4.38	12.4
	F	0.50	4.67	97	90	5.06	—1.2
"No chloride"...	G	0.05	3.76	83	59	5.30	—6.0
	G	0.50	4.74	97	90	5.06	—1.2
$(NH_4)_2SO_4$.....	H	0.05	3.22	68	30	7.34	—46.8
	H	0.50	4.70	94	80	5.56	—11.2
NaF.....	I	0.05	3.31	75	31	7.95	—59.0
	I	0.50	4.67	94	81	5.45	—9.0

TABLE II—*Continued.*

Effect of	Solution	Total Current Amp.	Current Ratio Obtained	Efficiency Per cent "n"	Efficiency Per cent "f"	Metal Ratio Obtained	Throwing Power Per cent
"All chloride" solutions:							
$NiCl_2$ *N*.....	J	0.05	3.25	92	80	3.73	25.4
	J	0.50	4.47	99	93	4.72	5.6
$NiCl_2$ *N*+ NH_4Cl 0.25 *N*..	K	0.05	2.93	91	78	3.42	31.6
	K	0.50	4.31	99	95	4.50	10.0
Additions:							
Sodium citrate...	L	0.05	2.99	82	60	4.08	18.4
	L	0.50	4.66	95	88	5.04	—0.8
Dextrin.....	M	0.05	3.06	86	65	4.02	19.6
	M	0.50	4.56	97	88	4.99	0.2
Hydrogen peroxide.....	N	0.05	1.93	40	4	22.10	—342.0
	N	0.50	4.59	84	51	7.69	—53.8
Sodium sulfite...	O	0.05	3.74	88	69	4.76	4.8
	O	0.50	4.43	94	92	4.55	9.0
Impurities:							
Cd.....	P	0.05	4.13	90	80	4.70	6.0
	P	0.50	4.79	98	91	5.13	—2.6
Cu.....	Q	0.05	2.93	90	73	3.60	28.0
	Q	0.50	4.61	98	92	4.88	2.4
Zn.....	R	0.05	3.40	88	68	4.44	11.2
	R	0.50	4.71	98	91	5.05	—1.0

nickel was employed as the anode. Experiments in which commercial nickel gauze containing about 2 per cent of manganese, or pure copper gauze, was plated with nickel and used as the anode, led in time to serious contamination of the solution. This was particularly the case when the copper gauze was used. Owing to the relative passivity of the pure electrolytic nickel, the copper or drawn nickel used as the base of the anodes dissolved, leaving a shell of pure nickel. However, the plated nickel gauze is satisfactory, provided the same solution is not used repeatedly.

The cathode efficiencies were measured, as before, by means of copper coulometers in series with the two cathode plates. The size of the copper cathodes in the coulometers was regulated so as to maintain the current densities upon them between 0.5 and 1.5 amp./sq. dm. When very small currents were employed, this necessitated the use of small copper wires as coulometer cathodes.

Avoidance of too low a cathode current density in the copper coulometer is a precaution which has been previously mentioned, but is frequently overlooked.

V. RESULTS OBTAINED.

The data secured in these experiments are recorded in Table II and Fig. 3, 4 and 5. Owing to the fact that the throwing power in nickel solutions is determined more by the efficiencies than by the current distribution ratios, the potentials involved in the latter are not included in Table II, though they are shown diagrammatically in Fig. 3.

The cathode efficiencies, recorded in Table II, are plotted in Fig. 4. The near plate is designated as "n"; the far, as "f." In Fig. 5, the throwing powers of typical solutions at various current densities are summarized.

VI. DISCUSSION OF RESULTS.

The significance of the above results may be conveniently considered from the standpoint of the specific variables involved. It will be observed that in some cases the throwing power is negative, that is, the metal distribution is less uniform than the primary current distribution, which corresponds to the shape of the object. The actual current distribution is, however, always more nearly uniform than the primary ratio.

Current Density.

In general an increase in current density causes the throwing power to approach zero, whether it is positive or negative at lower current densities. This is due to the fact that as the current density is increased the polarization and current efficiency each approach a constant maximum.

Temperature.

At low current densities an increase in temperature decreases throwing power. The current distribution is not thereby much changed, which is an evidence that the reduction in polarization is offset by the reduction in resistivity. The decrease in throw-

ing power is caused principally by a decrease in cathode efficiency[8] at the higher temperature.

Agitation.

Agitation of the solution at both cathodes, either mechanically or by air, causes a marked reduction in throwing power. This is due practically entirely to the reduction in cathode efficiency.

When a recessed article is moved through a solution, as upon a conveyor, or when solution is moved past it by any means, the most marked agitation usually occurs upon the exposed parts, upon which the current density is highest; and there is at least some tendency for the solution to be "pocketed" in the recesses. In order to simulate such conditions, "local" agitation was employed, the solution adjacent to the near plate being stirred mechanically, but not that at the far plate. The marked improvement in throwing power thus produced is due to the fact that the current efficiency at the near plate was reduced considerably, while that at the far plate was unchanged. In so far as these conditions are realized in a nickel plating tank, an improvement in throwing power may be expected. An obvious advantage of such agitation is that the use of a much higher average current density becomes possible, and the time required for plating is reduced.

Acidity and Nickel Concentration.

If the cathode efficiency is determined largely by the ratio between the effective concentrations of hydrogen ions and nickel ions in the cathode film, we would expect that it and consequently the throwing power should be decreased either by increasing the acidity (lowering pH) or decreasing the nickel concentration; and should be increased by decreasing the acidity or increasing the nickel content. The data in Table II confirm this prediction, and also show that such effects are due almost entirely to differences in the cathode efficiencies.

Substitutions for Ammonium Chloride.

In the "standard" solution (A) ammonium chloride is added principally to improve anode corrosion, though it also increases

[8] It must be borne in mind that in nickel deposition a change in cathode efficiency is always relatively greater at the lower current densities. It follows, of course, that throwing power varies directly with "cathode efficiency."

the conductivity. That it improves throwing power is evident from a comparison with the results obtained in solution G, which contained only nickel sulfate and boric acid. As practically identical results were obtained with equivalent amounts of the other chlorides, NaCl, $NiCl_2$ and $MgCl_2$ (solutions D, E, F), it is evident that the effect is due principally to the chloride ion, the presence of which increases the cathode efficiency, particularly at low current densities. The slightly lower throwing power with 0.25 *N* $NiCl_2$ (E) was caused by the lower conductivity of this solution, in which the nickel sulfate concentration was made only 0.75 *N* in order to keep a constant nickel content.

The beneficial effect of the chloride is emphasized by the poor results obtained with solutions H and I, containing instead of ammonium chloride, ammonium sulfate or sodium fluoride. In the latter solutions the cathode efficiencies at low current density are very low.

The poor throwing power of solutions containing fluorides confirms the experience of those engaged in commercial work.[9] In order to illustrate this effect, and also to check the validity of applying the results with the throwing power box to commercial practice, a few experiments were made with brass shaving soap boxes. These were cylinders closed at one end, about 3 cm. (1.2 in.) in diameter and 5.5 cm. (2.2 in.) deep. They were plated on racks under conditions approaching commercial practice, for a period of one hour in the "standard" solution (A) and in the fluoride solution (I), at an average current density of 0.05 amp./sq. dm. (0.46 amp./sq. ft.). The amount of nickel deposited on the inside upon and near the circular bottom (20 per cent of the total area) was removed by stripping with dilute hydrochloric acid (1 : 5), using a reversed current. The nickel in this solution was determined by dimethyl glyoxime precipitation. The results showed that in the "standard" solution the average thickness of the nickel deposited upon the bottom area examined, was 1.7 times that in the fluoride solution. In other words, it would require nearly twice as long to produce a deposit of a specified thickness upon the bottom of the box in a fluoride solution as in the "standard" solution. As it was impossible to measure or compute the primary distribution ratio upon the soap boxes,

[9] Private communication from G. B. Hogaboom.

the results represent simply a qualitative confirmation of the corresponding values for throwing power in Table II, *viz.*, 16.4 per cent and —59 per cent.

Nickel Chloride Solutions.

In view of the beneficial effect of chlorides in a nickel sulfate solution, we would expect nickel chloride baths to have good throwing power, which was found to be the case with solution J. The addition of ammonium chloride to the nickel chloride solution (K) decreased the resistivity, and still further improved the throwing power. The deposits obtained from the chloride solutions, especially those containing ammonium chloride, were darker than normal deposits. Further work will be required to determine whether the use of "all chloride" solutions would be justifiable where good throwing power is essential.

Additions to Nickel Baths.

It was impossible to study the effect of each of the many substances that have been proposed as additions to nickel baths, consequently only a few typical materials were examined.

Sodium Citrate. This salt is frequently added for nickel plating on zinc. The results show a good throwing power, which is due to the increased conductivity and polarization, and not to an improvement in cathode efficiency.

Dextrin. This substance may be considered as a typical colloidal addition agent. It is occasionally added to nickel baths, either as such or as an impurity in commercial glucose. The slight increase in throwing power, due to increased polarization, is not sufficient to warrant its use for this purpose. In general, nickel deposits are very sensitive to the effects of colloids, which should therefore be used carefully if at all.

Hydrogen Peroxide. This represents a typical simple oxidizing agent, the use of which has recently been recommended for preventing the formation of pits.[10] It is evident from the results that any such beneficial action is probably due to the fact that hydrogen, instead of being discharged, reduces the hydrogen peroxide. The extremely low throwing power in such solutions is caused by the

[10] C. P. Madsen, "Mechanically Perfect Electrolytic Nickel." Trans. Am. Electrochem. Soc., 45, 249 (1924).

fact that the reduction of hydrogen peroxide takes place at a much lower potential than the deposition of nickel, and hence the nickel cathode efficiency is greatly reduced at low current densities. With smaller concentrations of hydrogen peroxide, or with higher current densities, the efficiency and throwing power are much better.

Sodium Sulfite. In view of the striking decrease in cathode efficiency and throwing power in the presence of an oxidizing agent, it appeared probable that a reducing agent might be beneficial. Sodium sulfite was selected, because if completely oxidized it would form sulfate, which is a normal constituent of the solution. The few results obtained were favorable with respect to throwing power at the high current density; but the deposits were dark and unsuitable for commercial use. The data are included simply to show the desirability of a more detailed study of the effects of oxidizing and reducing agents in nickel deposition, which we hope to undertake in the near future.

Impurities.

Previous work[11] has shown that the most deleterious impurities likely to be present in nickel salts are copper and zinc. Cadmium has often been proposed as a "brightener" in nickel baths. As, however, the results which we have obtained show that its effects are similar to those of zinc, it may conveniently be considered with zinc and copper. These results are of interest not only because of their relation to throwing power, but also to the character of the deposits produced.

It will be noted that in the amounts used (0.001 *N*) both cadmium and zinc decrease the throwing power slightly. This is due to the formation of more nearly vertical I/e curves. Small amounts of copper improve the throwing power, because the I/e curves are more inclined, and because the metal cathode efficiency (including copper plus nickel) is increased at low current densities. The deposits produced from solutions containing 0.001 *N* cadmium were very spongy, alternately bright and gray, except at the higher current density (0.4 amp./sq. dm. or 3.7 amp./sq. ft.). At this current density the deposit was good, but brighter

[11] "The Effect of Impurities in Nickel Salts Used for Electrodeposition." M. R. Thompson and C. T. Thomas, Trans. Am. Electrochem. Soc., 42, 79 (1922).

than the normal deposit. The deposits from the solution containing 0.001 *N* zinc were entirely satisfactory and somewhat brighter than the standard deposits. The deposits containing copper were dark and spongy at the low current densities, but normal when the current density was increased. As the actual amounts of impurity deposited at high and low currents must be approximately the same, while the amount of nickel deposited is greater at the high current densities, it is to be expected that the most marked effect of the impurity would be observed in deposits formed at the lower current densities, because they contain the impurity in a higher ratio to the nickel.

In general, therefore, work requiring a low average current density, such as deeply recessed work, necessitates the use of purer anodes and solutions than when high current densities are used. Any operating condition such as heat, agitation, etc., which tends to increase the amount of impurity in the cathode film requires the use of materials of high purity.

These results are consistent with the experiments of Thompson and Thomas,[12] in which relatively high current densities (*e. g.*, 1 amp./sq. dm. or 9.3 amp./sq. ft.) were used, and hence higher concentrations of copper and zinc appeared permissible.

Cathode Potentials.

The cathode potentials obtained are illustrated in Fig. 3. In order to avoid confusion it was convenient to combine curves which coincided within the limit of error of the measurements. The curves for the deposition of nickel *only* are not shown (except in Fig. 1) because the hydrogen curves are considered more significant. The relative positions of the nickel and hydrogen curves determine the efficiency curves. (Fig. 4).

A few generalizations concerning the relative polarization expressed by the I/e curves are possible. It will be noticed that the polarization tends to vary directly as the H^+ content and inversely as the Ni^{++} content of the solution. The depolarizing influence of hydrogen peroxide is interesting. Comparison of the curve for nickel deposition only (with H_2O_2 present) with that of the "standard" solution shows that the same amount of nickel can be discharged at a much more positive potential in the presence of

[12] *Loc. cit.*

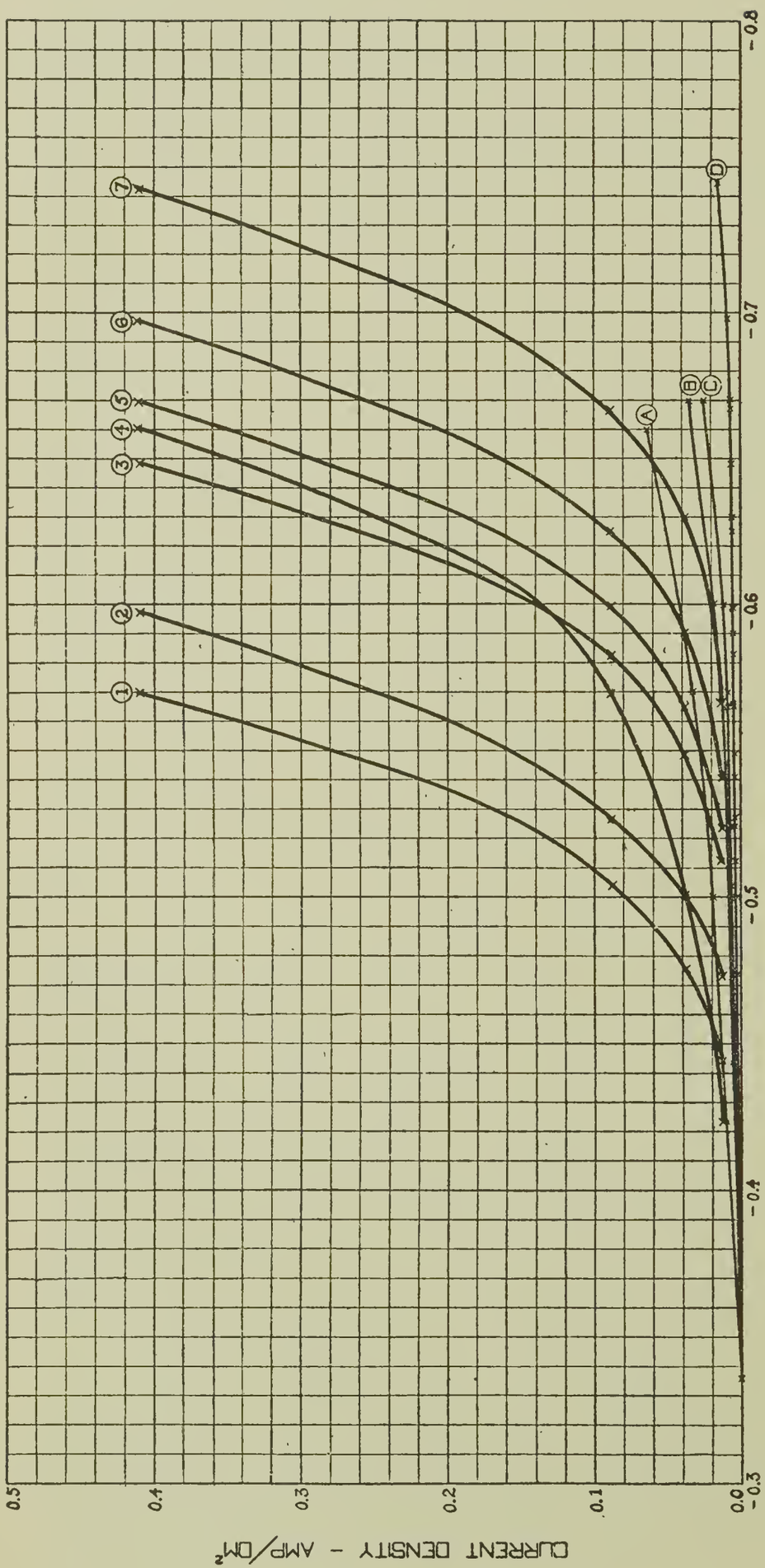


FIG. 3. Current Density-Cathode Potential Curves in Nickel Deposition.

Total Current Density Curves.

Curve:
1—Solution A at 45° C. (113° F.).
2—Solutions J and K ("all chloride").
3—Solution A at pH 6.5; C (2*N* Ni); F ($MgCl_2$); or E (0.25 *N* $NiCl_2$).
4—Solution N (H_2O_2).
5—Solution A with or without agitation; G ("no chloride"); D (NaCl); H ($(NH_4)_2SO_4$); or I (NaF).
6—Solution A at pH 4.5; or B (0.5 *N* Ni).
7—Solution L (citrate); or M (dextrin).

Hydrogen Discharge Curves.

Curve:
A—Solution N (H_2O_2).
B—Solution A agitated.
C—Solution A at 45° C. (113° F.); G ("no chloride"); H ($(NH_4)_2SO_4$); or I (NaF).
D—Solution A and others not included under curves A, B and C.

hydrogen peroxide. It will be further noticed that agitation does not (as with most metals) act as a depolarizer in nickel deposition. These and other phenomena offer strong circumstantial evidence that *the dynamic potential*[13] *of nickel co-deposited with hydrogen depends more upon the H-ion concentration of the cathode film than upon the Ni-ion concentration.*

Further evidence on this point is afforded by the I/e curve for deposition from the solution containing cadmium. This curve is not illustrated. In it the bottom of the "standard" curve (5) is displaced 0.10 v. to the right, while the upper part is practically unchanged. This is undoubtedly due to the fact that the presence of cadmium in the deposit influences its potential. A similar but smaller effect was obtained in the case of zinc, while copper displaced the bottom of the standard curve toward the left.

The effect of impurities can be readily explained when the potentials involved are considered. Copper, even in the low concentration here present, has a potential more positive than that of either nickel or hydrogen. Consequently it will tend to deposit first. This is the reason that even minute quantities of copper may lead to very inferior deposits, particularly at low current densities.

The potential of cadmium in 0.001 *N* cadmium solution is about —0.49 v., which potential is commonly reached in nickel deposition, even at relatively low current densities. Hence some cadmium will be deposited with the nickel and a poor deposit will result.

The static potential of zinc in 0.001 *N* zinc solution is about —0.85 v., a potential which is not ordinarily reached in nickel deposition, particularly at the low current densities. As a result there is practically no chance of depositing zinc as such, and thus securing a poor deposit. The fact that brighter deposits are obtained from the solutions containing zinc, is an indication that some zinc can be deposited as a zinc-nickel alloy before the discharge potential of zinc is reached. This phenomenon, which has been frequently observed, is analogous to the deposition of sodium on a mercury cathode.

It is well known that appreciable amounts of iron and cobalt can be present in a nickel deposit without having any marked

[13] The term "dynamic potential" is used here, as in the previous publication, to denote the potential of an electrode *during electrolysis.*

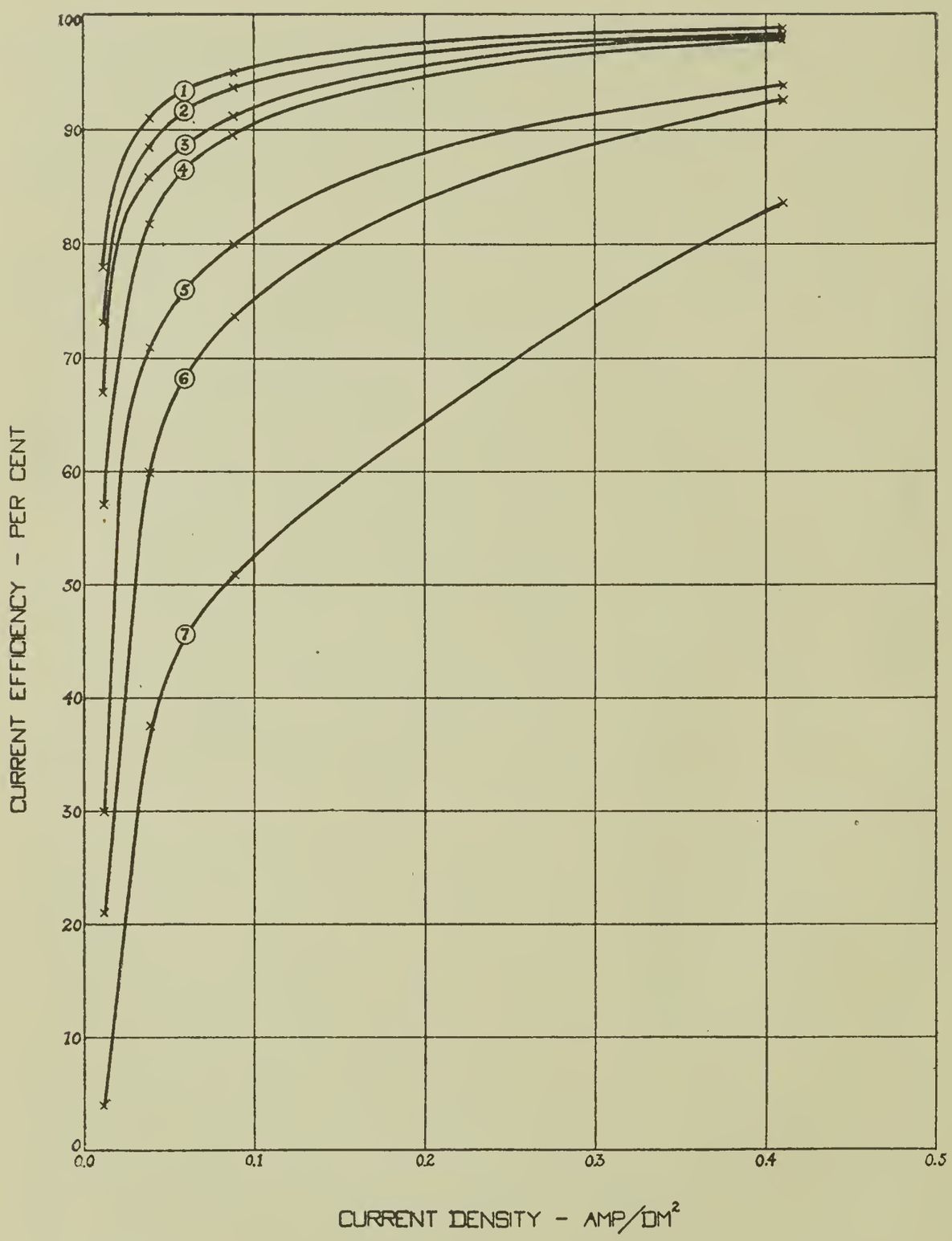


FIG. 4.

Cathode Efficiency Curves in Nickel Deposition.

Curve:

1—Solutions J and K ("all chloride").

2—Solution A at pH 6.5; C (2*N*-Ni) or E (0.25 *N* $NiCl_2$).

3—Solution A, D (NaCl); or F ($MgCl_2$).

4—Solution A at 45° or at pH 4.5; B (0.5 *N*-Ni); G ("no chloride"); L (citrate) or M (dextrin).

5—Solution H ($(NH_4)_2SO_4$) or I (NaF).

6—Solution A agitated.

7—Solution N (H_2O_2).

effects on its appearance. For this reason these impurities were not considered in this investigation. The fact that iron and cobalt are without effect is probably due to the overvoltage of hydrogen being practically the same on iron, cobalt, and nickel. Hence localized variations in hydrogen discharge and in the consequent structure of the deposit are impossible. The fact that the hydrogen overvoltage on copper, cadmium and zinc is higher than on nickel is reflected in the higher cathode efficiencies when these impurities are present in the deposit.

Cathode Efficiencies.

The importance of cathode efficiency in determining throwing power in nickel deposition is apparent. The close relationship between high efficiency and good throwing power is made evident by a comparison of Fig. 4 and 5. *Further improvement in the throwing power of the present type of nickel solutions is to be sought in improved cathode efficiency, particularly at low current densities.*

As stated previously, the cathode efficiency depends upon, (a) the equilibrium potentials of the metal and hydrogen in the solution, (b) the "effective" concentrations of metal ions and hydrogen ions in the cathode film, and (c) the overvoltage of hydrogen discharge upon the metal.

The most commonly accepted value for the normal potential of nickel[14] is —0.23 v., which value has however not been determined with so great an accuracy as that of most normal potentials. The difference of 0.23 v. between the nickel and hydrogen potentials applies however only to solutions in which the respective ion concentrations are normal. Actually most nickel deposition is conducted in nearly neutral solutions, with a pH of about 5 to 6. In a solution of pH 5.7, as used in most of these experiments, the static hydrogen potential is —0.34 v., while that of Ni (assuming 10 per cent dissociation of normal nickel sulfate) would be —0.26 v. Therefore, we might expect that nickel would deposit more readily than hydrogen and also that the cathode efficiency would *decrease* with increased current density, as in the case of the acid copper sulfate solution. The fact that the reverse

[14] F. Foerster, Elektrochemie Wässeriger Lösungen, 3d Edn. (1922).

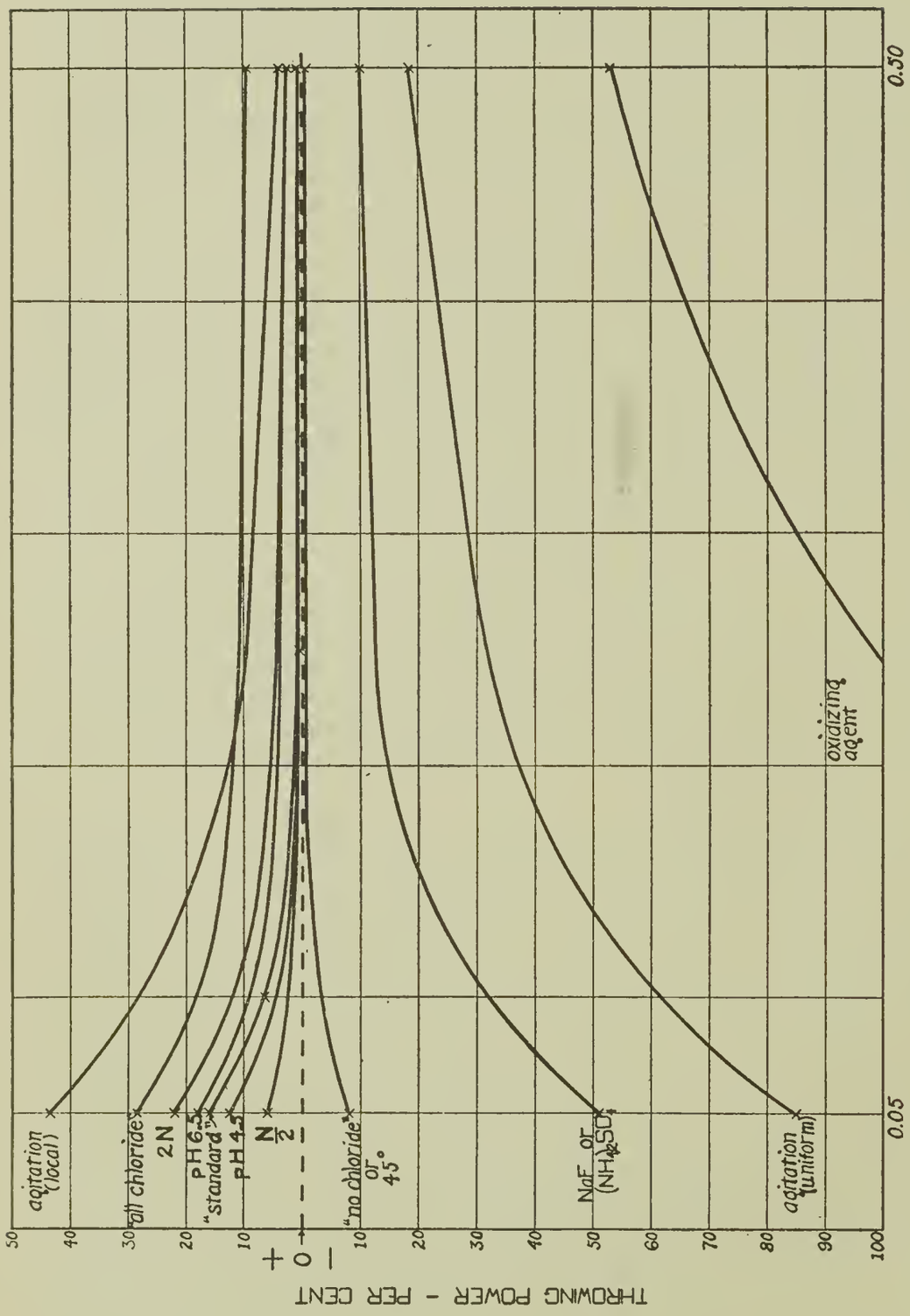


FIG. 5.
Throwing Power in Nickel Deposition.
The total current indicated was applied to two plates, each 10 x 10 cm., in the throwing power box, with a primary ratio of 5 : 1.

is true shows either that the normal potential of nickel is more negative than —0.23 v., or (as commonly supposed) there is some cause, such as "reaction resistance," which retards the separation of nickel until a potential more negative than its true potential is reached.

In the opinion of the author it is at least probable that the normal potential of nickel is more negative than —0.23 v. Further study will be required to decide which view is correct.

The static potentials of nickel and of hydrogen in a nickel solution can not be changed to any marked degree. A greater change can be produced in the dynamic potentials, that is, in the "effective" concentrations of nickel and hydrogen ions in the cathode films. No large change in the overvoltage of hydrogen discharge can be brought about, as the cathode in all cases is nickel soon after the beginning of electrolysis. The possible means of improving the efficiency and consequently the throwing power have thus been reduced to one factor—the ratio of the "effective" concentrations of metal and hydrogen ions in the cathode film.

This ratio depends upon that of the metal and hydrogen ion concentrations in the body of the solution, and upon the relative degrees to which these concentrations are reduced in consequence of discharge at the cathode. Thus, a discharge of hydrogen at the cathode must tend to reduce the hydrogen ion concentration in the cathode film, which therefore becomes less acid (or relatively more alkaline) than the body of the solution. The extent to which this occurs, and therefore the difference in the hydrogen ion concentrations of the film and the body of solution is determined by the *buffer* characteristics of the solution. The same term might with propriety be applied to the reduction in metal ion concentration brought about by discharge of metal ions. In both cases it expresses the rate of change of ion concentration upon dilution, modified by the effects of salts that may be present.

Any factor which will increase the ratio Ni^{++}/H^{+} *in the cathode film will increase throwing power.* Application of this principle offers an explanation for practically every result shown in Table II. Both heat and agitation tend to restore the most easily discharged of the two cations, that is, H^{+}, in the cathode film. In other words, the Ni^{++}/H^{+} ratio is decreased, and throwing power is decreased. A change in acidity or nickel concentration of the so-

lution is of course followed by a corresponding change in the Ni^{++}/H^{+} ratio in the cathode film. Increasing the chloride content increases nickel ion concentration through its effect on dissociation. Ammonium sulfate and sodium fluoride reduce the concentration of nickel ions owing to in the first case the "common ion effect," and in the second the effect of the fluoride ion on dissociation and possibly also the formation of complex ions. The effect of sodium citrate is probably due to the formation of complex ions. Another cause of the marked effect of fluorides upon the cathode efficiency is the decided buffer action upon the acidity in solutions containing fluorides and boric acid.[15] In consequence, in solutions with the same pH in the body of the solution the cathode film has a higher hydrogen ion concentration in the fluoride solution than in the "standard" solution. In general it appears desirable to have a moderate buffer action, such as is produced by boric acid, but not so much as is obtained with "fluoboric acid."

VII. CONCLUSIONS.

1. Throwing power in nickel deposition is determined by the same factors as in copper deposition. These are (a) the rate of change of cathode potential with current density, (b) the resistivity of the solution, and (c) the cathode efficiency at different current densities.

2. The chief factor in throwing power in nickel deposition is the cathode efficiency.

3. The cathode efficiency in any solution is determined by (a) the equilibrium potentials of the metal and hydrogen in the solution, (b) the "effective" concentrations of metal ions and hydrogen ions in the cathode film, and (c) the overvoltage of hydrogen discharge upon the metal.

4. The most significant factor entering into the efficiency of nickel deposition is the ratio of the "effective" nickel and hydrogen ion concentrations in the cathode film.

5. Throwing power is improved by a decrease in hydrogen ion concentration, or an increase in nickel ion concentration, in the cathode film, that is, an increase in the Ni^{++}/H^{+} ratio.

[15] "The Acidity of Nickel Depositing Solutions." M. R. Thomoson Trans. Am. Electrochem. Soc., **41**, 333 (1922).

6. Conditions which favor throwing power, through their effect on the Ni^{++}/H^{+} ratio are

(a) A high concentration of nickel salt in the solution.

(b) A solution of low acidity (high pH).

(c) The presence of a chloride in the solution.

(d) A moderately buffered solution.

(e) A low temperature.

(f) Agitation of the solution adjacent to the parts of the object receiving the highest current density.

7. An increase in current density causes the throwing power to approach zero, regardless of whether it is positive or negative at lower current densities.

8. Throwing power is decreased by oxidizing agents. Further work will be required before any conclusive statement regarding reducing agents can be made.

9. The presence of impurities in solutions used for the plating of recessed work, necessarily at low average current densities, is far more objectionable than in solutions used for rapid plating.

The author wishes to express his appreciation for the helpful advice and suggestions received from Dr. William Blum, under whose direction this research was conducted; also from George B. Hogaboom and the research committee of the American Electroplaters' Society.

DISCUSSION.

R. J. McKay[16]: The data presented, as is always the case with Dr. Blum's papers, are such as to be useful for reference in connection with other work. Dr. Blum, what is the exact mechanism of the effect of agitation on throwing power?

W. Blum[17]: The effect of agitation in a nickel solution is to change the ratio of the nickel and hydrogen ions in the film at the cathode. If we run a nickel bath at a pH of 5.8, the film at the cathode is not 5.8, but may, in an extreme case, be equal to 6.7,

[16] Supt. of Technical Service, International Nickel Co., New York City.
[17] Chemist, Bureau of Standards, Washington, D. C.

which is near the precipitation point of nickel hydroxide. We will get the maximum efficiency at a pH just before the precipitation of nickel hydroxide, when we have the maximum ratio of nickel to hydrogen ions.

If we agitate the solution, we bring up fresh hydrogen ions and thereby reduce this tendency for the cathode film to become less acid; consequently, the cathode efficiency is reduced. It is not a question of the speed of the nickel ions or nickel compounds past that point, but simply a question of replenishing hydrogen ions at the cathode as fast as they are used up. If we do not replenish them as fast as they are used up, then the solution becomes less acid, and may reach the point where nickel hydroxide is precipitated.

R. J. McKay: That is an interesting parallel to some of the conditions that exist in corrosion, and seems to be a logical explanation.

E. M. Baker[18]: It is interesting to note that two conclusions which are drawn from this paper are that moderate agitation in nickel plating solutions represents the best condition, and excessive agitation represents a bad condition, and that these conclusions are borne out in general knowledge of nickel plating practice. I think it is interesting also to note that the publications of Dr. Blum, and his co-workers of the Bureau of Standards, have been presenting principles which do a great deal to organize a mass of other information in the literature on plating in general.

A. H. Heatley[19] (*Communicated*): In reporting the interesting comparison of the throwing power of the standard and fluoride solutions, Mr. Haring states " . . . . it was *impossible* to measure or compute the primary distribution ratio upon the soap boxes . . . ." A method for measuring this ratio has been suggested, "by making up a cathode of the same shape from pieces of metal insulated from each other, with insulated leads for each."[20] If the soap box surface be divided into three parts, for example, the bottom and top halves of the inside and all the outside, mounted on a non-conducting box, six conductance meas-

[18] Asst. Prof. of Chem. Eng., Univ. of Michigan, Ann Arbor, Mich.

[19] Chemist, Roessler and Hasslacher Chemical Co., Niagara Falls, N. Y.

[20] A. H. Heatley, "Multiple Electrode Systems," Trans. Am. Electrochem. Soc., 44, 291 (1923).

urements would be required, using various combinations of leads as illustrated in Table I of the paper cited. The simplest form of Kohlrausch bridge would give sufficient accuracy. "The primary ratio is the ratio of the conductances leading from the anode to the various (sections of) cathode," in this case, d : e : f. The method can be extended to four or more sections of the cathode.

H. E. HARING (*Communicated*): In order to compute or measure the current distribution on different parts of an irregularly shaped article, such as a soap box, it would be necessary to isolate definite areas on each of which the current density is *uniform* or practically so. This could conceivably be accomplished, but not by any such simple means as Mr. Heatley has suggested. By the method which he has proposed, results would be obtained which would represent at best only approximately the primary distribution. Consequently any prediction of the metal distribution on an irregularly shaped object must be qualitative, or at best only semi-quantitative.

A paper presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 4, 1924, President Parmelee in the Chair.

INFLUENCE OF SULFUR, OXYGEN, COPPER AND MANGANESE ON THE RED-SHORTNESS OF IRON.[1]

By J. R. Cain.[2]

Abstract.

Small ingots, approximately 900 g. each, of electrolytic iron, and in some cases Armco ingot iron, were prepared in such a manner as to contain varying small amounts of sulfur, oxygen, copper and manganese, separately or in certain combinations. The ingots were melted under vacuum, or in an induction furnace under air. Bars forged from these were tested for red-shortness by bending back and forth over a blacksmith's anvil, while they cooled from approximately 1,100° to 500° C. It was found that if sulfur be below 0.01 per cent., there is no red-shortness, even when the oxygen content, as determined by the Ledebur method, is 0.2 per cent. If the sulfur be above 0.01 per cent, a manganese/sulfur quotient of 3.0 is sufficient to prevent red-shortness. The effect of copper was found to be of minor importance, but it had some tendency to correct red-shortness in the low sulfur materials (0.015 to 0.021 per cent S) studied.

I. INTRODUCTION.

Metallurgical literature and text-books contain many data on elements which are believed to cause or affect red-shortness of iron, that is, brittleness when worked above a red heat. Of the chemical elements usually present in commercial iron and steel, sulfur, oxygen and copper are most often blamed. It is quite generally accepted that sulfur, in the absence of necessary amounts of manganese, causes red-shortness. The minimal per-

[1] Manuscript received July 11, 1924. Published by permission of the Director of the Bureau of Standards.

[2] Research Associate, Bureau of Standards.

centage of sulfur at which red-shortness disappears, has, however, not been accurately fixed. Many writers consider oxygen equally potent in causing brittleness during hot working, although many statements to the contrary can be found. The effect of copper is probably most disputed by various investigators.

A summary of the literature and of the views on effects of different elements on the red-shortness of iron is given by Howe.[3] The discordance of views with respect to the effect of different elements is quite evident from Howe's summary, particularly from a table given on page 92, showing working properties of various unrecarburized basic open-hearth and acid bessemer steels in which oxygen contents above 0.068 per cent are reported. As stated by Howe, much uncertainty attaches to the oxygen results given in his table. In fact, many of them were admittedly only approximations, because no reasonably satisfactory methods for determining this element in iron and steel had been devised at that time. Howe says: "It is stated that more than 0.1 per cent oxygen appreciably affects forgeableness, but that in smaller proportions it is often harmless; I do not, however, think we have evidence to warrant precise statements." Also, "At the end of the Bessemer process the metal usually absorbs a certain proportion of oxygen, which renders it unforgeable." Ledebur[4] states that 0.10 per cent oxygen in mild steel causes red-shortness. Stoughton[5] writes: "There is probably no constituent more harmful to steel than oxygen * * * The effect of oxygen is somewhat similar to that of sulfur, and, in common parlance, makes the steel 'rotten.'"

Among other investigators of the effect of oxygen on red-shortness and other properties of iron may be mentioned, W. Austin,[6] Eichoff,[7] Becker,[8] Oberhoffer and d'Huart[9] and Herbert Mon-

[3] Metallurgy of Steel, Second ed. (1891).

[4] Eisenhütterkunde, First ed., 1, 296, and 3, 12.

[5] "Metallurgy of Iron and Steel," Third ed. (1923).

[6] Wesley Austin, "The Influence of Oxygen on Some Properties of Pure Iron," J. Iron and Steel Inst., 2, 157-163 (1915).

[7] Prof. Eichhoff-Charlottenburg, "Ueber die Fortschritte in der Elektrostahl Darstellung"; Stahl u. Eisen, 27, 48 (1907).

[8] E. Becker, "Ueber das Zustandsdiagram Schwefeleisen—Eisen und den durch Schwefel hervorgerufen Rotbruch"; Stahl u. Eisen, 32, 1017-1021 (1912).

[9] P. Oberhoffer and K. d'Huart, "Beiträge zur Kenntnis oxydischer Schlackeneinschlüsse sowie der Desoxidationsvargaenge in Flusseisen"; Stahl u. Eisen, 39, 165-169 and 196-202 (1919).

den.[10] Fleming[11] discusses briefly the effect of oxygen content and deoxidation on the rolling properties of commercially pure irons.

Howe (*loc. cit.,* p. 44) discusses the effect of manganese in preventing red-shortness, and states "* * * * it (manganese) moreover counteracts hot-shortness, no matter at what temperature and from what cause it may arise, whether from P, S, Cu, Si, iron oxide, suspended silicate of iron or blow-holes * * *" He gives tables showing forging results on samples of steels and irons from various sources where the ratio of manganese to sulfur or other elements to which red-shortness might be attributed varies greatly, and there is also great variation in the forging results. He says: "* * * as we have neither a scientific basis for calculating the quantity of residual manganese needed to prevent hot-shortness under given conditions, nor even trustworthy empirical data, the steel maker has to proceed tentatively when under unusual conditions."

Among those who have investigated the effect of copper on red-shortness may be mentioned Eggeytz,[12] Wasum,[13] Choubley,[14] Stead and Evans,[15] and Campbell,[16] all of whom regard copper, *per se,* as of minor significance in causing red-shortness, although some of them believe that, in combination with a high sulfur content, copper may help to cause red-shortness. On the other hand, Brustlein,[17] Howe (*loc. cit.,* p. 82), Ruhfus,[18] Sargent,[19] and Richardson and Richardson[20] are inclined to regard copper as an element likely to cause red-shortness in iron and steel, regardless

[10] H. Monden, "Beitrag zur Metallurgie des basischen Siemens-Martin Verfahren und zur Frage des Einflusses des Sauerstoffgehaltes auf die mechanischen Eigenschaften des Flusseisens insbesondere des Rotbruches"; Stahl u. Eisen, **43**, 745-752 and 782-788 (1923).

[11] W. R. Fleming, "Oxygen in Iron and Steel; Value of Existing Methods for its Determination," Proc. Amer. Soc. for Testing Materials, **13**, 477-486 (1913).

[12] Jahresbericht, Wagner, p. 9 (1882).

[13] Stahl u. Eisen, **1**, 193 (1882); Abstract in J. Iron and Steel Inst., **1**, 369 (1882).

[14] Bul. Soc. Industrie Minerale, **23**, 205 (1884); Abstract in J. Iron and Steel Inst., **1**, 248 (1884).

[15] J. E. Stead and John Evans, "The Influence of Copper on Steel Rails and Plates," J. Iron and Steel Inst., **1**, 89-100 (1901).

[16] Manufacture and Properties of Iron and Steel, p. 358 (1907).

[17] See Howe (*loc. cit.,* p. 368).

[18] A. Ruhfus, "Der Einfluss des Kupfers auf Eisen," Stahl u. Eisen, **20**, 691-692, (1900).

[19] George W. Sargent, "Iron-Copper Alloys"; Metallurgical and Chemical Engineering, **8**, 68 (1910).

[20] E. A. Richardson and L. T. Richardson, "The Influence of Copper, Manganese and Chromium and Some of Their Combinations on the Corrosion of Iron and Steel"; Trans. Am. Electrochem. Soc., **38**, 221-223 (1920).

of other elements present. Aupperle, in discussing Richardson's paper, states that if the sulfur content is low, amounts of copper up to 0.5 per cent do not cause red-shortness.

II. EXPERIMENTAL METHODS.

In reviewing the work of previous investigators one is impressed by the difficulty of their problem, in that, although they usually attempted to determine the effect of one element on iron, they were constrained to use commercial steels for their experiments. However careful the selection of these specimens, it was, and still is, almost impossible to select compositions in which only one element at a time varies in a regular manner.

Considerations such as these led to the research described herein, which differs from most of the preceding work on the subject, in that the samples were made specifically for the investigation in small electric furnaces, which could be kept under fairly good control. As recorded in Table I, electrolytic iron was used as raw material, except for certain experiments on manganese-sulfur ratios. The advantages of such raw material with its well-known low content of copper, manganese and sulfur is obvious. The analysis of the electrolytic iron used was, in per cent, C, 0.004, S, 0.004, Si, 0.001, Cu, Ni and Co together 0.014, P, trace.

In planning this investigation the intent has been to limit the study, for the present, to the effect of sulfur, oxygen, copper and manganese on red-shortness of iron, in such manner that the major effect of an element could be studied alone, or in the presence of a desired amount of another element. It is practically impossible, of course, to have only one of these elements combined with iron to the complete exclusion of the others; it is also impracticable, without an undue amount of work, to study all the possible combinations of these elements with iron, nor does this seem necessary in view of what follows.

The samples were melted in the carbon resistor vacuum furnaces described in a previous investigation by Neville and Cain[21] and in a high frequency induction furnace. The former type of furnace enabled samples to be melted with practical exclusion of air, hence permitted a fairly good control of oxygen content,

[21] R. P. Neville and J. R. Cain, "Preparation and Properties of Pure Iron Alloys: I. Effects of Carbon and Manganese on the Mechanical Properties of Pure Iron"; Bureau of Standards Sci. Paper 453, Oct. 16, 1922.

although there was occasional slight contamination of the melts by silicon, from impurities in the crucible material, and carbon. On the other hand, the melts made in the induction furnace under air are generally characterized by high content of oxygen, but contain only very small percentages of carbon, silicon and manganese.

Magnesia crucibles were used as containers in both furnaces. Melts made in the Arsem furnace were allowed to solidify in the crucible under vacuum. Melts made in the induction furnace sometimes solidified in the crucible and others were poured into chill molds. The average weight of the ingots used was around 900 g. Ingots which solidified in the crucibles were about 3.5 cm. diameter, and 10 cm. long with a slight taper. Ingots made in chill molds were about 3.5 cm. square and 8 to 9 cm. long.

The electrolytic iron used for the work has been described in the paper last cited. The manganese was that produced commercially by aluminum reduction, and was over 98 per cent pure. The copper was over 99.9 per cent pure.

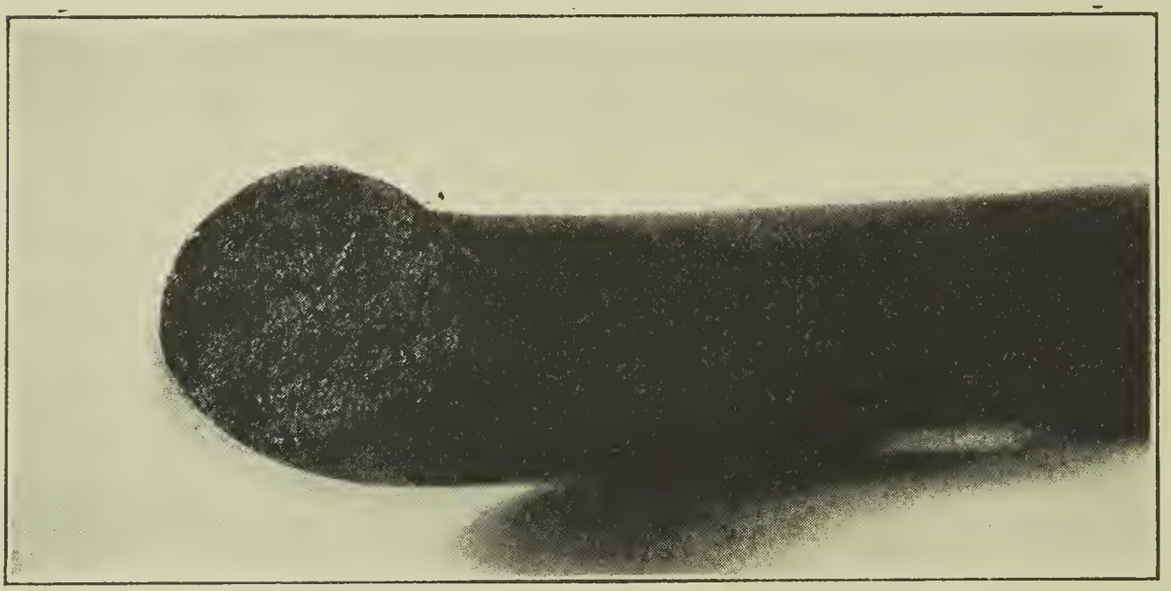
Preparatory to making the red-shortness test the ingots were forged to 1.27 cm. (0.5 in.) round bars. The test for red-shortness consisted in heating the bars to approximately 1,100° C. in a gas-fired or coke-fired forge, withdrawing the bars quickly from the fire and bending them back and forth rapidly through 180° over the sharp edge of an anvil while they cooled rapidly to a dull red heat. The bending was done with a hammer heavy enough to apply the necessary force, but light enough so that the operator could make the bends quickly.

In this way a sample could be subjected to perhaps a dozen bending cycles, provided it did not break because of red-shortness. A sample free from red-shortness stands such a test without breaking; one which is red-short breaks off with a fracture like that shown in Fig. 1. The temperature at which the fracture takes place varies, probably within a range of 100° to 200° C. for different specimens of variable composition, but no attempts were made during this work accurately to fix the temperature of breaking, since this would have necessitated the devising of special mechanism.

It was observed that the samples would usually stand the bending test above and below the brittle range, where any brittleness

existed. During the preliminary forging of the bars to 1.27 cm. (0.5 in.) sections, whether the ingots were worked under a press or a hammer, it was found that samples which afterwards proved red-short in the anvil bending test could, in many cases, be worked throughout the brittle range, without serious cracking or breaking.

Chips from the broken test bars were analyzed for the ordinary constituents by the methods of the American Society for Testing Materials, or slight modification of these. Oxygen was determined by the Ledebur method, from unsieved chips cut at slow speed on a milling machine. The work of Cain and Pettijohn,[22]



x 100

Fig. 1.

Typical Red-Short Fracture. 0.017 Per Cent C; 0.034 Per Cent O_2; 0.033 Per Cent S.

and of others, has shown that the Ledebur method can be applied with a fair degree of accuracy to pure irons or commercially pure irons. These investigations have shown that in a low-carbon iron the iron oxide inclusions are determined with a fair degree of accuracy, provided necessary precautions are taken to secure fine chips free from surface oxidation, and a rapid current of pure hydrogen is used. On the other hand, the limitations of such a method as applied to ordinary steels, should be noted, particularly as applied to specimen 85, Table I.

Micrographs of specimen 543 (Fig. 2), 0.09 per cent C and

[22] J. R. Cain and Earl Pettijohn, A Critical Study of the Ledebur Method for Determining Oxygen in Iron and Steel; Bureau of Standards Tech. Paper No. 118, Jan. 11, 1919. See particularly page 23 as to cutting samples in air.

0.018 per cent O, and specimen 587 (Fig. 3), 0.02 per cent C and 0.176 per cent O, show the irregular distribution, also the size of the oxide particles in the latter.

TABLE I.

Composition of Samples and Results of Forging Tests.

No.	Per Cent C	Per Cent Si	Per Cent Mn	Per Cent Cu	Per Cent S	Per Cent O_2	Forging Test	Quotient Mn/S
Electrolytic Iron Used for Preparing These Ingots.								
12	0.010	0.01	0.012	0.007	0.009	0.051	O. K.	1.3
543	0.090	0.08	0.006	0.006	0.006	0.018	O. K.	1.0
544	0.110	0.08	0.001	0.004	0.004	0.034	O. K.	0.25
73-1	0.050	0.04	0.006	0.003	0.007	0.037	O. K.	0.9
587	0.020	....	0.001	0.005	0.003	0.176	O. K.	0.3
588	0.020	....	0.001	0.005	0.004	0.147	O. K.	0.25
231	0.020	....	0.002	0.005	0.005	0.200	O. K.	0.4
75-1	0.025	0.02	0.006	0.003	0.014	0.036	Broke	0.4
77-1	0.045	0.02	0.004	0.002	0.022	0.036	Broke	0.2
74-1	0.060	0.05	0.001	0.045	0.016	0.028	O. K.	0.06
31	0.018	0.02	0.008	0.060	0.018	0.040	O. K.	0.4
32	0.022	0.06	0.018	0.168	0.015	0.020	O. K.	1.2
33	0.015	0.05	0.027	0.365	0.015	0.023	O. K.	1.8
34	0.031	0.08	0.021	0.526	0.017	0.021	O. K.	1.2
85	0.490	0.04	0.020	0.045	0.021	0.038	Broke	1.0
Commercially Pure Iron Used for Preparing These Ingots								
A 510	0.066	....	0.033	0.022	0.015	0.030	O. K.	2.2
A 511	0.033	0.05	0.031	0.023	0.011	0.027	O. K.	2.8
3	0.034	0.10	0.150	0.033	0.029	0.028	O. K.	5.5
76-1	0.060	0.05	0.120	0.099	0.034	0.027	O. K.	3.5
A	0.010	0.01	0.090	0.040	0.023	0.085	Broke	3.9
B	0.010	0.00	0.160	0.037	0.050	0.109	Broke	3.2

Only traces of phosphorus were present in these samples.

III. DISCUSSION.

Samples 543, 544 and 73.1 of Table I contained less than 0.01 per cent each of manganese, sulfur and copper, with oxygen less than 0.04 per cent in each; these samples were free from red-shortness. On the other hand, samples 75.1 and 77-1, with about the same content of manganese, oxygen and copper as those just mentioned, but with 0.014 per cent and 0.022 per cent of sulfur, respectively, both broke on the red-shortness test. This indicates that sulfur, and not oxygen, is the cause of the red-shortness in

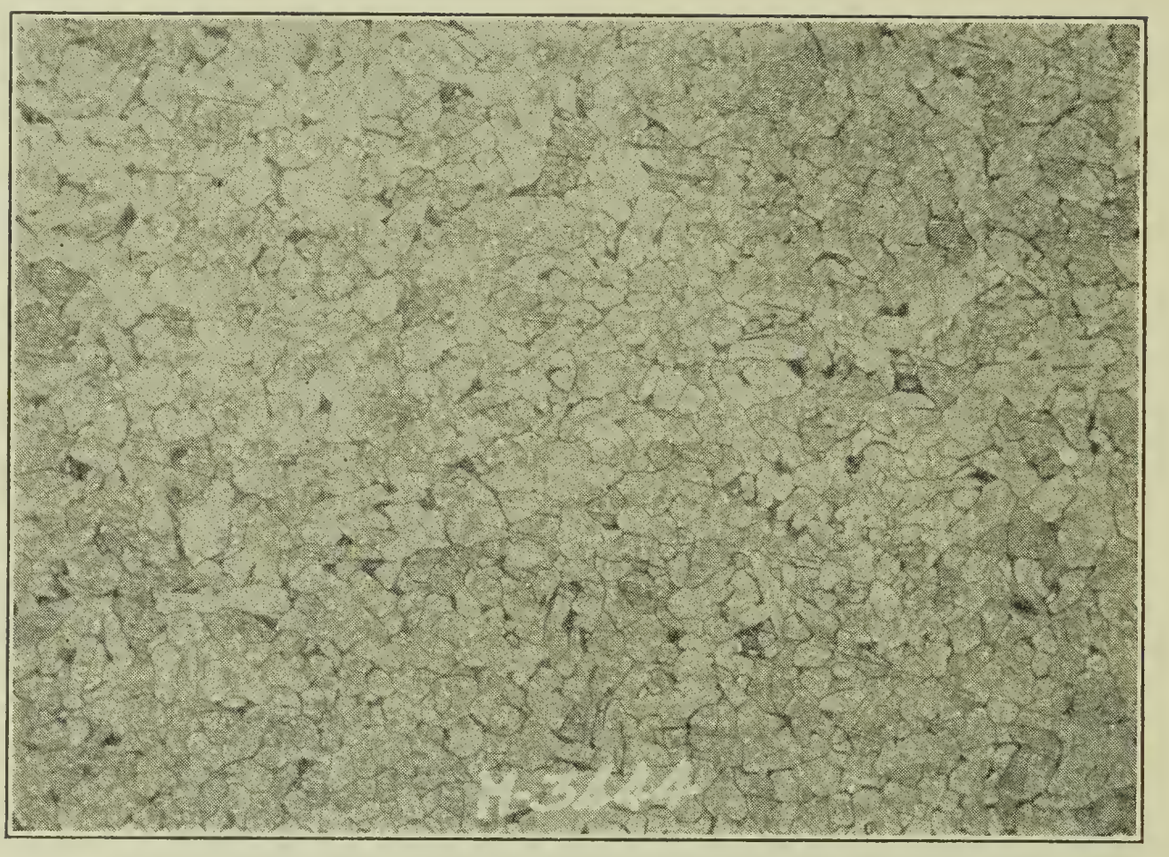


FIG. 2. Specimen 543. x 100
Absence of Iron Oxide Inclusions. 0.09 Per Cent C; 0.018 Per Cent O_2; 0.006 Per Cent S.

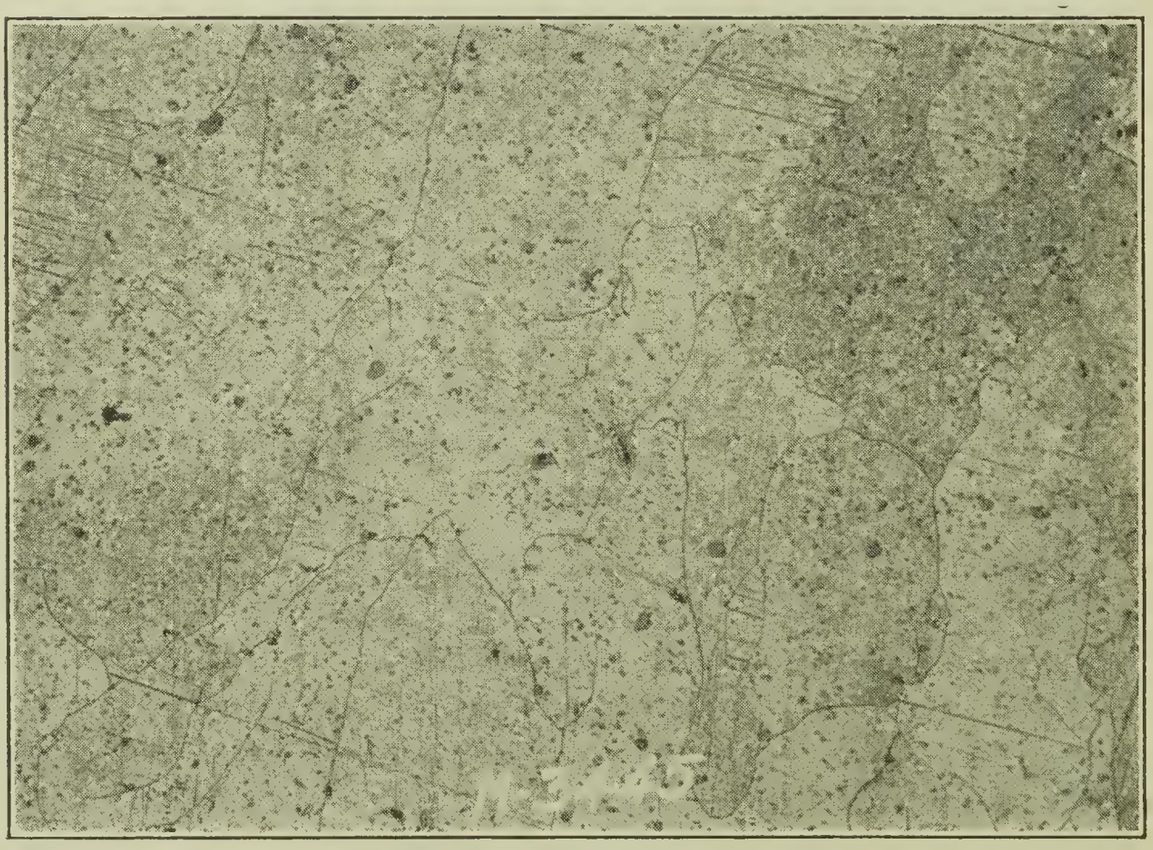


FIG. 3. Specimen 587. x 100
Iron Oxide Inclusions. 0.020 Per Cent C; 0.176 Per Cent O_2; 0.003 Per Cent S.

these samples, and that the percentage of sulfur where red-shortness disappears lies between 0.014 and 0.007 per cent.

Samples 12, 587, 588 and 231 carry less than 0.01 per cent of copper and sulfur and (except sample 12 with 0.012 per cent Mn) less than 0.01 per cent Mn; that is, they contain well below the limiting percentage of sulfur for causing red-shortness; however, it will be noted that they carry very large percentages of oxygen (0.05 to 0.20 per cent). Nevertheless, none of them broke on the red-shortness forging test. This indicates that a very high oxygen percentage in pure iron does not cause red-shortness, if the sulfur content is below 0.01 per cent. There is, however, an apparent effect of oxygen when manganese has been added to correct red-shortness, due to sulfur, as stated below.

The samples with increasing copper content, 74-1 and 31 to 34, inclusive, contain small percentages of manganese, oxygen and sulfur (0.015 to 0.018 per cent of the latter). Although sulfur is present in these samples considerably in excess of the amount that has been mentioned as the safe limit for preventing red-shortness (below 0.01 per cent), nevertheless none of these samples broke during the anvil test for red-shortness. Examination of the manganese content of these samples shows, in the light of what follows, that the red-shortness could not have been prevented by manganese, since the latter element was present in such small amounts.

It would seem, then, that copper up to 0.5 cent in such material tends to prevent red-shortness. It will be noted, however, that sample 85 is an exception; this sample contains a large amount of carbon in comparison with the other samples of Table I, and this may explain the exception, since it has been found by most investigators that amounts of carbon, such as found in steels, profoundly affect the properties of the iron-copper system. Evidently, considerable more investigation would be needed if it were desired to ascertain whether copper tends to correct red-shortness when the percentage of sulfur and carbon vary considerably from the samples herein described.

Among the samples containing varying amounts of manganese relative to sulfur, where the sulfur is above 0.01 per cent, the lowest ratio found at which red-shortness was absent was $Mn/S = 2.2$ (sample A 510). Specimen A 511, with a quotient of

Fig. 4. Specimen 587, Unetched. x 100

Fig. 5. Specimen 543, Unetched. x 100

2.8, checks this result. Both of these ingots contained low percentages of oxygen and copper. Sample 3 had a considerably higher percentage of sulfur than the two specimens just mentioned, and with a manganese/sulfur quotient of 5.2 was not red-short. As yet no complete series has been made with wide variations in the percentage of sulfur or in the manganese/sulfur quotients. This may be studied in another phase of this investigation.

The recent work of Feild[23] shows that a Mn/S quotient of 3.6 is necessary in order to secure satisfactory hot rolling properties (per cent C, 0.42; per cent S, 0.075; per cent Mn, 0.28; per cent Cu, not given); with quotients lower than this the rolling results were unsatisfactory on 10 other compositions. Feild also refers in this paper to the necessary Mn/S quotient of between 3 and 5 established by the work of Hackney[24] and to the researches of McCance[25] on the equilibrium of the reaction between ferrous oxide and manganese, which is supposed to represent what takes place in deoxidation by manganese.

Samples A and B were highly oxidized due to exposure to air in melting, and both broke in the anvil test, even though the manganese-sulfur ratio was considerably higher than was the case for A 510 and A 511. A possible explanation is that part of the manganese found by analyses in these samples was present as oxide, and hence would not be effective for preventing red-shortness. It is not impossible, also, in oxidized samples such as these, that oxysulfides of iron, such as described by E. D. Campbell,[26] or eutectics of oxides of iron with sulfides of iron or manganese (see Becker, *loc. cit.*) are present, and the phenomena in such cases with respect to red-shortness or with respect to manganese added as a corrective for red-shortness might be quite different. The views advanced by Sargent (*loc. cit.*) as to the possible effect of oxides of copper on red-shortness in low-carbon irons and steels are also of interest in considering these results.

In applying the results of this work to ordinary irons and

[23] Alexander L. Feild, "Effect of Zirconium on Hot-rolling Properties of High Sulfur Steels and the Occurrence of Zirconium Sulfide"; Preprint 1306-S (17 pp.); February, 1924, meeting of Amer. Inst. of Mining and Metallurgical Engrs.

[24] Hackney, Discussion of paper by M. F. Gautier, "The Use of Ferro-Manganese," J. Iron and Steel Inst., p. 63 (1876).

[25] Andrew McCane, "Non-Metallic Inclusions; Their Constitution and Occurrence in Steel," J. Iron and Steel Inst., 97, 239-286 (1918).

[26] E. D. Campbell, "On the Diffusion of Sulfides Through Steel," Amer. Chem. J., 18, 707-719 (1896).

steels, it should be noted that most of the compositions given in Table I are quite different from any commercial product. This is particularly true of those samples having sulfur contents below 0.01 per cent, since it is very difficult and expensive to manufacture such a product commercially. The samples with very high oxygen content (0.10 per cent and above) are also abnormal in comparison with the oxygen of commercial irons and steels reported in recent investigations.

These deviations from commercial practice were made intentionally during this investigation, in order to establish the various points in respect to the effect of composition on red-shortness, but it is not intended to imply thereby that the compositions herein described are practical or even advantageous. It should be noted, also, that such factors as the mass law, the rate of cooling, segragation and slag cleansing action may profoundly affect the distribution, crystallographic habit and form of chemical combination of the elements investigated, so that the relationships in large masses of metal such as are used industrially, might be quite different in some cases from those described in this paper. With these qualifications, however, it is believed that the experiments described will help to throw light on some of the disputed matters affecting red-shortness.

IV. SUMMARY.

The effects of sulfur, oxygen, copper and manganese on the red-shortness of pure iron have been investigated in a series of small experimental ingots. The results of this investigation indicate that:

1. Sulfur is the principal element responsible for red-shortness. In order to avoid red-shortness in iron not more than 0.01 per cent sulfur should be present.

2. Oxygen in amounts up to 0.20 per cent does not cause red-shortness in pure iron if the sulfur is below 0.01 per cent.

3. Manganese may prevent red-shortness in iron when present to the extent of three times the sulfur percentage, if the oxygen percentage is not above 0.04.

4. The presence of considerable amounts of oxygen in irons (0.10 per cent and above) tends to reduce the efficiency of man-

ganese in preventing red-shortness. The hypothesis is advanced that this is because some of the manganese reported in such irons is present as oxide.

5. Copper (0.05 to 0.5 per cent) is of minor importance in its effect on red-shortness of pure iron, but in some of the specimens described in this paper it tended to decrease the red-shortness.

The author wishes to express appreciation for co-operation and assistance in this investigation from his associates in the divisions of metallurgy and chemistry of the Bureau of Standards, and from the research department of the American Rolling Mill Company.

Washington, D. C.,
April 15, 1924.

DISCUSSION.

B. D. SAKLATWALLA[27]: In experiments of this nature we should give consideration to the fact that when you add sulfur or sulfides to an already purified iron in an induction furnace, the effect of such sulfur is different from residual sulfur from a refining process. The presence of the residual sulfide is a barometric indication of the incomplete refining of the steel. So, while you might have the same sulfur content in the two cases, such content is no indication of the quality of the steels. It appears that the presence of oxygen has much to do with deleterious properties we have ascribed to various impurities. In a recent number of the Journal of the Iron and Steel Institute of Great Britain the National Physical Laboratory reports that alloys were prepared of iron and iron oxide, and that the iron oxide content itself was found to be rather harmless, which corresponds to the ideas expressed in Mr. Cain's paper. It is the *indirect* effect of the oxides that is harmful. Zirconium and manganese tend to counteract the effect of sulfur, owing to their deoxidizing power, and because they allow the sulfides and probably also phosphides to coagulate by easier passage through the deoxidized steel and get into a harmless state.

[27] Vanadium Corp. of America, Bridgeville, Pa.

In ascribing ill effects, therefore, to sulfur or any single element, the secondary phenomena of the elimination of oxygen and nitrogen should be taken into consideration.

J. R. CAIN (*Communicated*): In reply to Dr. Saklatwalla, it should be noted that no sulfur was added to any of the small melts described in my paper. When the sulfur content of the ingots made with electrolytic iron was greater than that of the electrolytic iron itself (0.004 per cent) this was caused by impurities derived from the magnesia or zirkon crucibles or from the furnace atmosphere. This applies also to the commercially pure iron used for making the ingots with varying manganese-sulfur ratio.

It seems quite possible that oxygen may exert a secondary effect on red shortness, in destroying any manganese, zirconium or other metal that might otherwise combine with the sulfur and thus prevent its embrittling action. I have called attention to this possibility in my paper, and have referred to Ingots A and B, which were highly oxidized and in which manganese did not correct red shortness, although the manganese-sulfur ratio indicated by ordinary methods of anaylsis was sufficient to prevent red-shortness. It is not improbable that a great deal of the manganese in over-oxidized steel is present as manganese oxide, which, of course, would not be available for prevention of sulfur red-shortness. Until we have chemical and metallographic methods for determining manganese oxide in steels and irons, these questions cannot be settled definitely. The results of Monden[28] may possibly be explained in this way.

A possible effect of nitrogen in causing red-shortness has also been mentioned in an interesting paper by J. Kent Smith.[29] In my samples made from electrolytic iron, there could have been very little nitrogen, hence those which were red short could not have been so from this cause, especially those melted *in vacuo*.

The work of the National Physical Laboratory confirms some of the results reported in my paper. It is interesting to note, also, that researches on nickel conducted at the Bureau of Standards by Merica and Waltenberg show that sulfur and oxygen in nickel

[28] The research is mentioned in my paper; his work has also been abstracted in Iron Age, **114**, 1338 (1924).

[29] Iron Age, **114**, 1209 (1924).

affect this metal in a manner analogous to their effects on iron, as I have described. Nickel seems to be even more sensitive to small amounts of sulfur than iron. This work, I understand, is soon to be published.

The results of small furnace experiments must be interpreted with caution when applied to large scale operations, but when such interpretation is used it would seem that data from small melts, made under better control than can be hoped for in industrial operations, may be helpful in iron and steel metallurgy.

A paper presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 4, 1924, President Parmelee in the Chair.

THE PREPARATION OF PURE ALLOYS

Including a Preliminary Study of Certain Electrical Properties of the System Aluminum-Magnesium.[1]

By Robert Franklin Mehl.[2]

Abstract.

The accuracy of metallographic data is discussed, with particular reference to the effect of impurities upon electrical measurements. Sources of contamination are pointed out, and the various methods are discussed by means of which contamination has heretofore been avoided. The preparation of pure basic oxide crucibles is discussed and a new method of making pure magnesia crucibles of high strength and density, for use up to 1,200° C., is given. A combined furnace and casting apparatus is described for the preparation of very pure alloys in a form suitable for the measurement of electrical properties. Methods for the measurement of the thermo-electromotive force and the temperature coefficient of resistance of aluminum-magnesium alloys are given. The results of preliminary measurements of the temperature coefficient of resistance and of the thermo-electromotive force and its temperature coefficient, upon certain compositions of the system Al-Mg, are presented.

Some of the properties of the binary metallic alloys vary almost linearly with the composition, even in alloys of the solid solution types, whereas other properties, especially electrical conductivity and thermo-electromotive force often change with extreme rapidity, and the values observed are in consequence greatly affected by errors in the composition. In cases in which one of

[1] Contribution from the Chemical Laboratory, Princeton University. Manuscript received March 10, 1924.
[2] Dept. of Chemistry, Juniata College, Huntingdon, Pa.

the component elements dissolves the other in the solid state, the addition of the first few parts per cent of the solute element alters both of the quantities named in particularly marked degree. The magnitude of this displacement, at least in the case of conductivity, appears to depend upon the relative positions of the two elements in the periodic table, being greatest when the elements occupy positions remote from each other.[3] Thus while the effect of the addition to cobalt of one per cent of nickel is very small, the conductivity of iron is lowered 48 per cent by one atom per cent of carbon; a like proportion of silicon diminishes the conductivity of copper by 64 per cent; and in the case of tin and gold the effect reaches 77 per cent.[3] Similarly the conductivity of copper is lowered 30 per cent by 0.1 per cent of arsenic.[4] And since the influence of the solute diminishes with increasing concentration, the effects of smaller additions are proportionally even larger.

It is because of these facts that contamination during melting is of great importance in connection with the measurement of the electrical properties of alloys. Most of the contaminating elements likely to be introduced into the alloy from the crucible or the atmosphere in which it is melted are distinctly non-metallic, including Si, C, S, P, O and N, and these, being in general far removed in the periodic table from the metals with which the experimenter is concerned, may thus be expected to introduce considerable errors into the measurements of the electrical properties.

That such errors are indeed present is well recognized. Guertler,[5] for example, pointed out that data upon electrical conductivity available in 1908 were not to be trusted to within 5 per cent, and that differences of 10 per cent between the results of different investigators were not unusual. Although there have been great advances in the knowledge of the alloys since this estimate was written, it cannot be said that the situation with regard to the accuracy of electrical data is much better at the present time.

In view, therefore, of the theoretical interest which more exact values would possess, and of the fact that the other errors which

[3] A. L. Norbury, Trans. Faraday Soc., 26, 570 (1921).

[4] W. R. Whitney, Trans. Am. Electrochem. Soc., 21, 23 (1912), referring to papers by Addicks, Hofmann and others.

[5] W. Guertler, Jahrbuch Radioaktiv. Elektronik., 5, 17-323 (1908).

enter into their determination are of lower orders of magnitude, the preparation of alloys of the highest purity possible, and the investigation of the electrical properties of such materials would seem to be highly desirable.

The work here described consisted in a study of the methods designed to lessen the principal difficulties in the making of such alloys, contamination from the crucible, and contamination from the atmosphere during melting and casting; and in a study of binary aluminum-magnesium alloys prepared by the methods arrived at. The results upon the system aluminum-magnesium relate to only a few compositions, and are in this sense merely preliminary. A more comprehensive study of the series is already well advanced.

CRUCIBLES FOR ALLOY INVESTIGATION.

The amount of impurity introduced into an alloy by the crucible may be considerable. Fireclay crucibles have been favored among investigators largely because of their mechanical strength. For the preparation of pure alloys, however, where silica is objectionable, they are out of the question. The same is true of crucibles made of porcelain, Marquard mass, impervite or alundum. For metals melting under 1,100° (with the probable exception of Al), graphite has proved itself very valuable. It also, however, usually contains some silica; and with the higher-melting metals it forms carbides.

In general, the best crucible for metallographic investigation is one in which the molten alloy comes into contact with a pure basic oxide alone. In this type the oxide may constitute the whole crucible or may be used as a lining ("brasqueing") for a crucible of other material.[6, 7] In the latter case the purity of the oxide is combined with the strength of the containing crucible but the method is of doubtful dependability, due to the tendency of the lining to crack.

The refractories zirconia, alumina and magnesia are most suitable for pure crucibles because of their high melting points: magnesia, 2,800°; alumina, 2,050°; zirconia, 2,500-2,950°.[8] It is a

[6] R. S. Hutton and J. E. Petaval, Electrochem. and Metallurg. Ind., 6, 104 (1908).
[7] H. C. Greenwood, Chem. News, 100, 49 (1909).
[8] Alfred Stansfield, The Electric Furnace: Its Construction, Operation and Uses. New York, 1914.

difficult task, however, to prepare crucibles of these oxides without any binder.

A summary of the investigations which have been reported upon the making of zirconia crucibles has been given by J. W. Marden and M. N. Rich in a recent publication.[9] Work by Podszus[10] is extensively quoted by Marden and Rich, and deserves special mention here, as does the work of O. Ruff and G. Lauschke.[11] Zirconia appears to be in certain respects the best adapted of all the oxides to the manufacture of high-temperature crucibles, its other advantages being enhanced by the fact that it lacks the troublesome tendency to hydrate, which is shown by magnesia. To make crucibles from zirconia, however, temperatures above 2,000° are required, which constitutes an unnecessary difficulty when very high temperatures are not demanded by the work for which the crucibles are to be employed. This is in large degree true also of mixtures of zirconia with other refractory oxides, such as beryllia, alumina, thoria and yttria.

Comparatively little work appears to have been done upon the making of crucibles from pure alumina, probably because this material does not promise any such advantages as belong to magnesia or zirconia. A small alumina crucible, in most respects suitable for experimental work, is now commercially available; but it is bonded with silica and hence is unsuited to work in which it is sought to prepare alloys free from silicon.

Processes for the manufacture of magnesia crucibles have been described by Yensen,[12] Watts,[13] C. F. Burgess and Aston,[14] Ferguson,[15] and Cain, Schramm and Cleaves.[16] In all of the various processes the purified magnesia is first shrunk by heating to a temperature near 1,600° C., then ground and pressed into a mould under high pressure, and finally heated to a point at which sintering sets in, with consequent cohesion of the rather coarse particles of MgO.

[9] J. W. Marden and M. N. Rich, Investigation of Zirconium with Especial Reference to the Metal and Oxide. Dept. of the Interior, Bureau of Mines. Bulletin 186, 1921.

[10] E. Podszus, J. Soc. Chem. Ind., **36**, I, 217 (1917).

[11] O. Ruff and G. Lauschke, Zeitsch. anorg. Chem., **87**, 198 (1914).

[12] T. D. Yensen, Trans, Amer. Electrochem. Soc., **32**, 176 (1917); also Trans. Amer. Ceram. Soc., **1**, 730 (1918).

[13] O. P. Watts, Wisconsin Eng., **17**, 64.

[14] C. F. Burgess and J. Aston, Trans. Amer. Electrochem. Soc., **15**, 369 (1909).

[15] J. B. Ferguson, Trans. Amer. Ceram. Soc., **1**, 439 (1918).

[16] J. R. Cain, E. Schramm and H. E. Cleaves, Bureau of Standards, Scientific Paper No. 266 (1916).

Of the various crucibles described by these writers some, notably those of Cain, Schramm and Cleaves, were of very high purity, and others seem to have possessed excellent mechanical strength. But it does not appear that any of the methods of manufacture yielded crucibles which possessed both of these desirable qualities. Strength, where it was obtained, seems to have been due to the bonding action of silica.

It was therefore decided with equipment generally available to attack anew the problem of making magnesia crucibles which should be both strong enough to meet all ordinary requirements, and of a very high order of purity. A brief indication of the experiments which finally led to a successful process may afford information of service to other experimenters in similar fields and is therefore here included.

Magnesia, when made into a plastic mass either with water alone or with aqueous solutions such as those of dextrine or glucose, undergoes hydration. The subsequent dehydration, during the baking and firing of the crucibles was found invariably to cause shrinkage and cracking. This difficulty was not obviated by the addition of an agent such as cryolite intended to bond the magnesia at higher temperatures. Attempts to form dry magnesia, under very high pressures, into masses which could be fired without shrinkage were unsuccessful, but seemed to indicate that such a procedure might be feasible if a form of mould could be devised which would distribute the pressure with some approach to uniformity.

Plastic masses of magnesia mixed with various dispersions of organic adhesives, such as dextrine, tragacanth, mastic or shellac, in non-aqueous liquids, such as ethyl alcohol, acetone, chloroform and benzene, did away with the difficulty of shrinkage, since they prevented hydration; but the resulting magnesia ware was extremely friable in all cases except one. The one exception forms the basis of the procedure finally employed for making crucibles, which is as follows:

C. P. "heavy magnesia," of as high a degree of purity as can be obtained or prepared, especially free from silica, is dried and shrunk by heating to 1,200° C., for one hour. It is then kept closely stoppered until used. A fairly thick syrup of shellac in absolute alcohol, from which the sediment has been allowed to

settle, is employed to form with the dried magnesia a mixture which will pack readily into the mould, and yet is not too plastic. The mixture quickly assumes a pink color, which in the course of a few minutes deepens to a magenta tone upon surfaces exposed to the air. The crucible still in the mould is next somewhat hardened by blowing air into it for several hours at the ordinary temperature. It is then removed from the mould and baked for several hours more in an air oven, at a temperature of from 100° to 130°. After this process the mass, although still of a light purplish color, is sufficiently hard to be handled without concern and may even be ground down to thin-walled form upon the

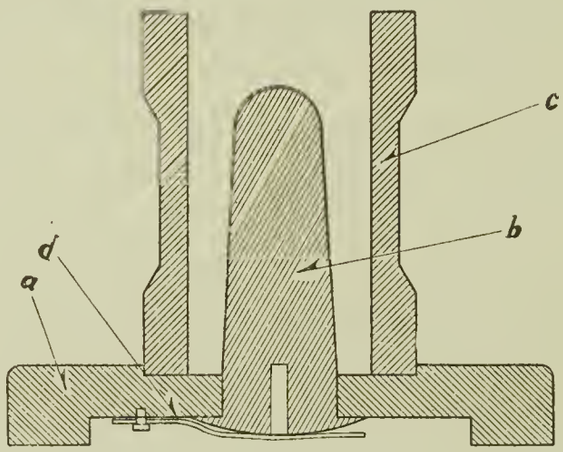


Fig. 1. Mould for making magnesia crucibles.

emery wheel, although this operation is better deferred until after firing. The firing is conducted in an electric furnace by bringing the crucible gradually to a temperature of 1,200° C. in the course of two or three hours and allowing it to cool slowly. During the firing all organic matter is burned out and the crucible resumes a snowy-white color, since it contains at the end of the operation nothing except pure magnesia. It is nevertheless satisfactorily hard, and may now be ground down upon the emery wheel from the thick-walled form which is most readily molded to a wall thickness of five or six millimeters, without the exercise of more than ordinary care. It is very fine-grained, and of much the consistency of chalk. Since no shrinkage takes place, the crucible has after being fired, the form and dimensions given it by the mould. The completed crucible must be kept in a desiccator until used, since exposure to moist air results in hydration.

The rôle played by the shellac binder in the formation of these

crucibles is somewhat in doubt. Possibly a more or less crystalline compound ("resinate") is produced, which breaks down on firing, leaving a coherent skeleton of magnesia. This would be analogous to the conversion of cellulose into charcoal. Whatever the real explanation, the fact is plain that the shellac binder, and this alone of all that have been tried in these experiments, produces a magnesia mass of high mechanical strength.

The work upon these crucibles is being continued and already gives reasonable assurance that they can be made even stronger, and adapted to temperatures much above 1,200°. As here described they already offer a crucible which is readily made, in which any of the lower melting metals can be melted without contamination, and which is strong enough to be handled without special care, and to support the weight of the molten charge.

The mould employed is shown in Fig. 1. It is of brass and consists of a base *a*, the core *b*, the divided barrel *c*, the spring clip *d*, and a key. The cover and base are recessed to receive the barrel, and the base is also provided with a slightly tapered opening into which the core is inserted from below. The core is held in place during molding by the clip *d*, and is withdrawn by means of the key, which screws into the hole in the bottom of the core.

Before use, the surfaces of the mould and core which are to be in contact with the crucible are covered with two layers of thin wax paper, dipped in heavy petroleum machine oil. The paper is applied in narrow strips, in order that it may conform to the curved surfaces, and has been found very efficient in preventing adhesion.

In molding, the plastic mass, in as dry a state as is feasible, is tamped into the mould from above. The core, and after this the base, are then taken off and the crucible is subjected to a preliminary drying of several hours in a brisk current of air before the barrel is removed. If several crucibles are to be made at once, it is therefore necessary to provide a barrel for each. A single base and core serve for all.

VACUUM CASTING FURNACE.

In order to melt and cast alloys in the form of rods suitable for electrical measurement without exposing them in the heated

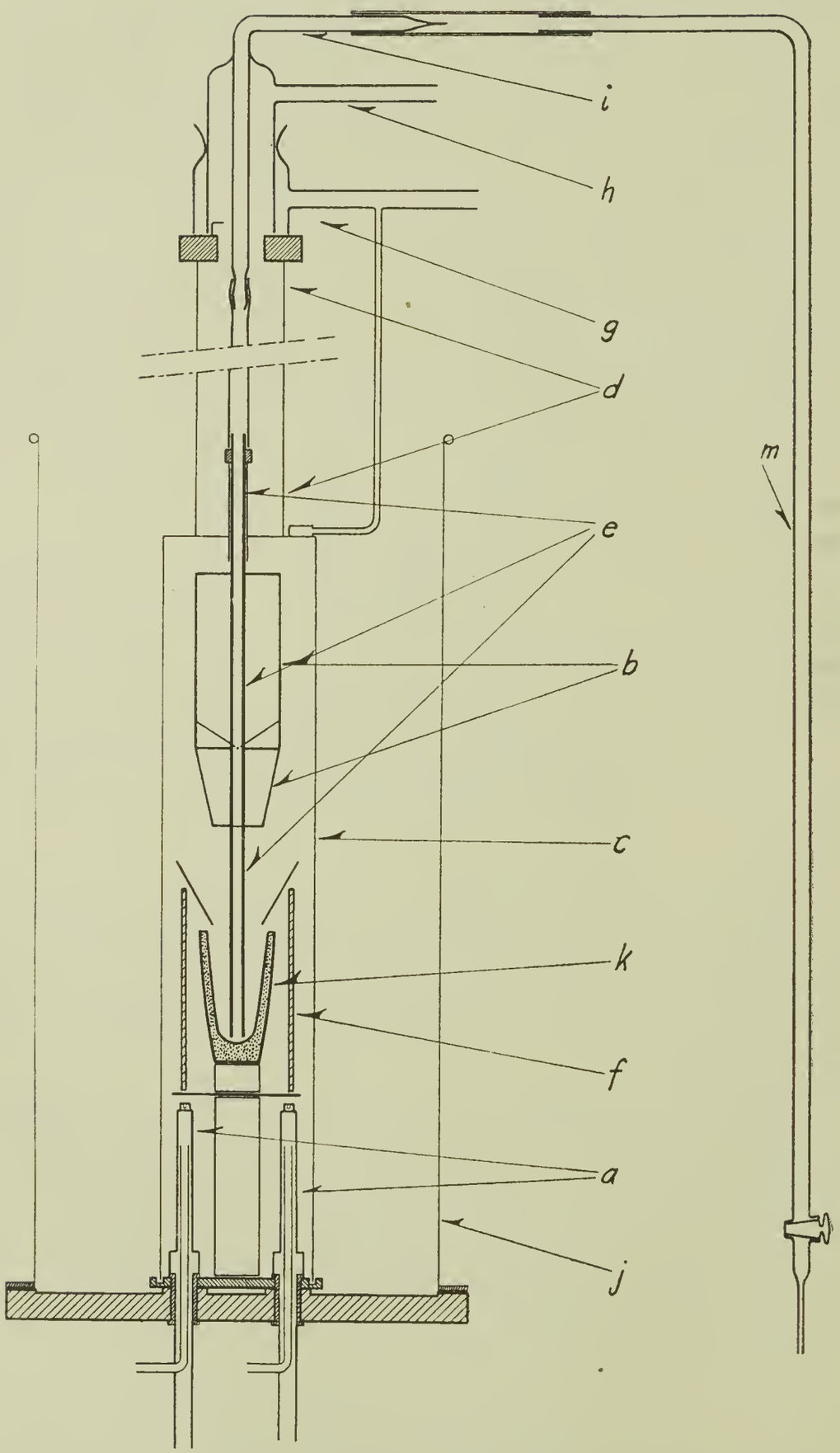


FIG. 2. Furnace for casting alloys uncontaminated by air.

condition to the action of the atmosphere, the furnace was developed which is shown in Fig. 2.

It consists essentially of the following parts: A metal base, through which pass the insulated, water-cooled electrodes, *a;* a chute and hopper, *b,* in which the charge is retained while the crucible is freed from gases; a jacket, *c,* with extension, *d,* in which the mould-tube, *e,* is suspended until the casting is to be made; a heater, *f,* of resistance wire supported upon a refractory cylinder; and a glass head, *g.* This head carries a side tube, *h,* which connects with the pump, the gauge and the supply of inert gas, and another outlet *i,* through which suction is applied to the mould-tube to draw the molten metal up into the latter. The connection between the outlet, *i,* and the top of the mould-tube, *e,* is made by a length of thin-walled pure gum tubing, which remains coiled in until the mould is dropped, and which is prevented from collapse by the support given it from within by a closely-wound helix of thin copper wire. The mould-tube is shown in Fig. 2 in the position for drawing up the molten alloy, the lower end projecting into the crucible, *k.* The rubber tube is accordingly uncoiled; for purposes of diagramming, the extension tube, *d,* is sectioned—its actual length is 47 cm., whereas the length of the jacket is 43 cm. The other parts shown in Fig. 2 are all drawn in proportion. The furnace is surrounded by the water packet, *j.*

The operations necessary to melt and cast an alloy are the following: The metals are placed in the hopper, *b,* which is kept closed by a fuse wire; the jacket and head are placed in position, and the junctions made tight by means of a resinous cement; the outlet, *i,* is sealed off as shown in Fig. 2; the side tube, *h,* is joined to the glass pump system; and the furnace is evacuated. When a good vacuum has been produced, the heater is brought to its highest temperature, and the heating and pumping are continued for some hours in order to free the crucible and adjacent portions of the apparatus as completely as possible from adsorbed gases, occasional readings being meantime taken with a McLeod gauge. When a satisfactory "hot vacuum" (0.001 mm. Hg) has been secured, the apparatus is filled with the inert gas, after being first allowed somewhat to cool if the metals to be melted are very volatile. The fuse which controls the hopper is then blown, permitting the charge to enter the crucible, and the alloy is melted and kept in

a state of fusion for a few minutes to bring about complete mixing. The heater current is then turned off, and the fuse which suspends the mould-tube, *c,* is blown, causing the mould to drop to a position such that it dips deeply into the melt. Connection is then established between the outlet, *i,* and a tube containing mercury, *m,* and by allowing the level of the latter to fall a predetermined distance, the molten alloy is drawn up into *e* to the desired height.

There are several details about the apparatus which, while not essential, have greatly facilitated the operation of the furnace and should therefore have some mention.

Hopper *b,* with its chute, is supported on a steel tripod screwed to the metal base of the furnace. It was found necessary to keep the chute this distance from the furnace in order to prevent premature blow-outs of the fuse which kept shut the doors of the hopper. When this separation is not made, stray currents perversely jump from furnace to chute, causing the fuse to be blown and therefore the run to be ruined. This fuse makes one connection to the tripod and thus to the furnace base, and the other connection is made through a glass tube to one electrode, so that the fuse can be blown by shorting a suitable current across furnace base and electrode.

On the top of the furnace, *f,* rests a silver funnel which serves to direct all of the charge coming from the hopper into the crucible. It is necessary, of course, that every particle of the weighed-out charge reach the crucible if a predetermined alloy composition is to be obtained.

During the operations previous to casting the greater part of the mould-tube, *e,* is retained in the extension tube. It is held in this position by a fuse attached to the collar on the top of the mould-tube and to the small steel-rod "gallows" on the end of the steel extension tube, *d.* This fuse makes electrical connection through a glass seal in the glass head, *g,* and through the mould-tube which is in contact with the jacket, *e,* at the junction of *c* and *d.*

The resinous cement used to join the extension tube to the glass head and to seal the quartz window to the top of the furnace jacket gave some trouble in the formation of small leaks difficult to locate. This trouble was completely eliminated by the use of

a guard vacuum, operated by a mechanical pump of large capacity. The construction of these double seals is shown in the figure.

It is important that crucible, *k,* be kept in the center of furnace, *f,* in order that all parts of it receive equal heating. Were this not the case, colder parts would retain adsorbed gas which could be imparted to the molten alloy in the subsequent operations.

PREPARATION OF PURE ALLOY RODS OF ALUMINUM-MAGNESIUM.

The system chosen for this investigation was aluminum-magnesium. It seemed especially adapted, first, because its components are very reactive and would subject a method of preparation to a severe test; second, because its fusion demanded only moderately high temperatures and for this reason would not entail, in the early stages of development, the difficulties peculiar to high-temperature work; third, because the constitution of the system is of much present interest and is still uncertain in some important respects, despite recent investigation; and, finally, because starting materials of exceptional purity could be obtained.

Starting Materials.

The aluminum was that supplied by the Bureau of Standards for the calibration of thermo-couples, and was certified to have a melting point of 658.7° From information contained in Circular No. 66 of the Bureau, this material has approximately the following composition:

	Per Cent	
Iron	0.18	The aluminum having been found by difference, and other elements than those named not having been sought.
Silicon	0.15	
Copper	0.004	
Manganese	Trace	
Carbon	0.01	
Aluminum	99.66	

The magnesium was of a quality which has been rendered available only by recent industrial advances. It was obtained from the American Magnesium Corporation of Niagara Falls and had been made by processes of which the last consisted of distillation *in vacuo,* so that the metal as received was composed of beautiful idiomorphic crystals protruding from a crystalline mass.

Tests in the laboratory of the manufacturers were reported to have shown the metal "to be free from impurity," and careful

examination in the course of the present work failed to detect any traces of iron, potassium, calcium or silicon. A fugitive odor of hydrocarbon, produced when the crystalline mass was broken, indicated the presence of a small amount of carbide; and scattered through the crystals were small flakes of carbon which were easily removed by mechanical means.

Crucibles.

The crucibles employed were of magnesia, made in the manner already described. For their preparation it was desirable to have material of as high a degree of purity as possible, and particularly free from silica because of the readiness with which the metals which were to be melted react with this substance.

Unfortunately silica is not one of the impurities to which attention appears to be directed by the manufacturers, and no magnesia now readily obtainable is wholly satisfactory for the purpose here considered. After examining samples of "C. P. Heavy Magnesia" from various sources, a lot was selected which appeared to contain less silica than any other, and for which the dealers' analysis in respect to other impurities was as follows:

	Per Cent
Chloride	0.003
Sulfate	None
Iron	0.0005
Alumina	0.009
Carbonate	3.09

From the fact that the aluminum-magnesium alloys produced in crucibles of this material showed only quantities of silica which were approximately such as would result from the 0.15 per cent of silicon in the aluminum used, it may be concluded that this particular lot of magnesia was as pure as need be demanded. It is unfortunate, however, that there is not available a material prepared by calcination of the fluoride, or by some other method well adapted to eliminate silica.

Furnace.

The furnace used for melting and casting the alloys was one which has already been described in general terms, and which was indeed developed in the study of these alloys. It may be remarked that the hopper and chute, constituting the portions of

the apparatus with which the metals came in contact before entering the crucible, were of sheet nickel, a material selected because of the facility with which it could be kept clean, and that a "ceiling" of the same material was suspended in the upper part of the furnace jacket to protect the crucible and its contents from particles of rust, etc., which might otherwise have fallen in.

Mould.

The choice of a mould-tube suitable for aluminum-magnesium alloys was a matter of some difficulty. Tubes of silica, porcelain, or similar materials were not permissible, and any of the ordinary metals seemed likely to react with the melt. Since the liquidus temperatures, within the range of compositions to be studied, did not exceed 480°, and casting could be effected at a temperature only a few degrees higher, it was thought that a metal of very high melting point would not react noticeably during the brief time for which it must be in contact before solidification occurred, and a tube of molybdenum was therefore obtained. It was found, however, that the casting adhered very firmly to the molybdenum, and could not be removed unbroken from the mould.

The tube finally adopted was of seamless steel, 37.5 cm. long, with a wall thickness of 1.6 mm. It had an inside diameter of 6.5 mm. throughout its upper half, increasing uniformly in the lower half to 7.8 mm. at the bottom. In order to prevent reaction with the molten alloy, and to facilitate removal of the casting, it was coated inside with a thin, adherent deposit of soot, produced by drawing through it the smoke from a flame of illuminating gas enriched with benzene.

From the results of several previous investigators it seemed unlikely that the protective coating of soot would react with aluminum-magnesium alloys under the conditions obtaining in this work. Thus Weston and Ellis[17] reported that the presence of air is necessary to the interaction of carbon with either aluminum or magnesium; Pring[18] stated that no trace of aluminum carbide could be found after heating the elements together for twenty hours at 600°, and that magnesium and carbon do not react when heated *in vacuo;* and from Novak's[19] statements regarding the

[17] F. E. Weston and H. R. Ellis, Trans. Faraday Soc., **4**, 60 (1908).
[18] J. N. Pring, J. Chem. Soc., **93**, 2101-8 (1908).
[19] J. Novak, Zeitsch. physikal. Chem., **73**, 513-46 (1910).

carbides of magnesium it may be concluded that less than 0.10 per cent of the combined carbides would be formed by heating magnesium with carbon (sugar charcoal), at the temperature

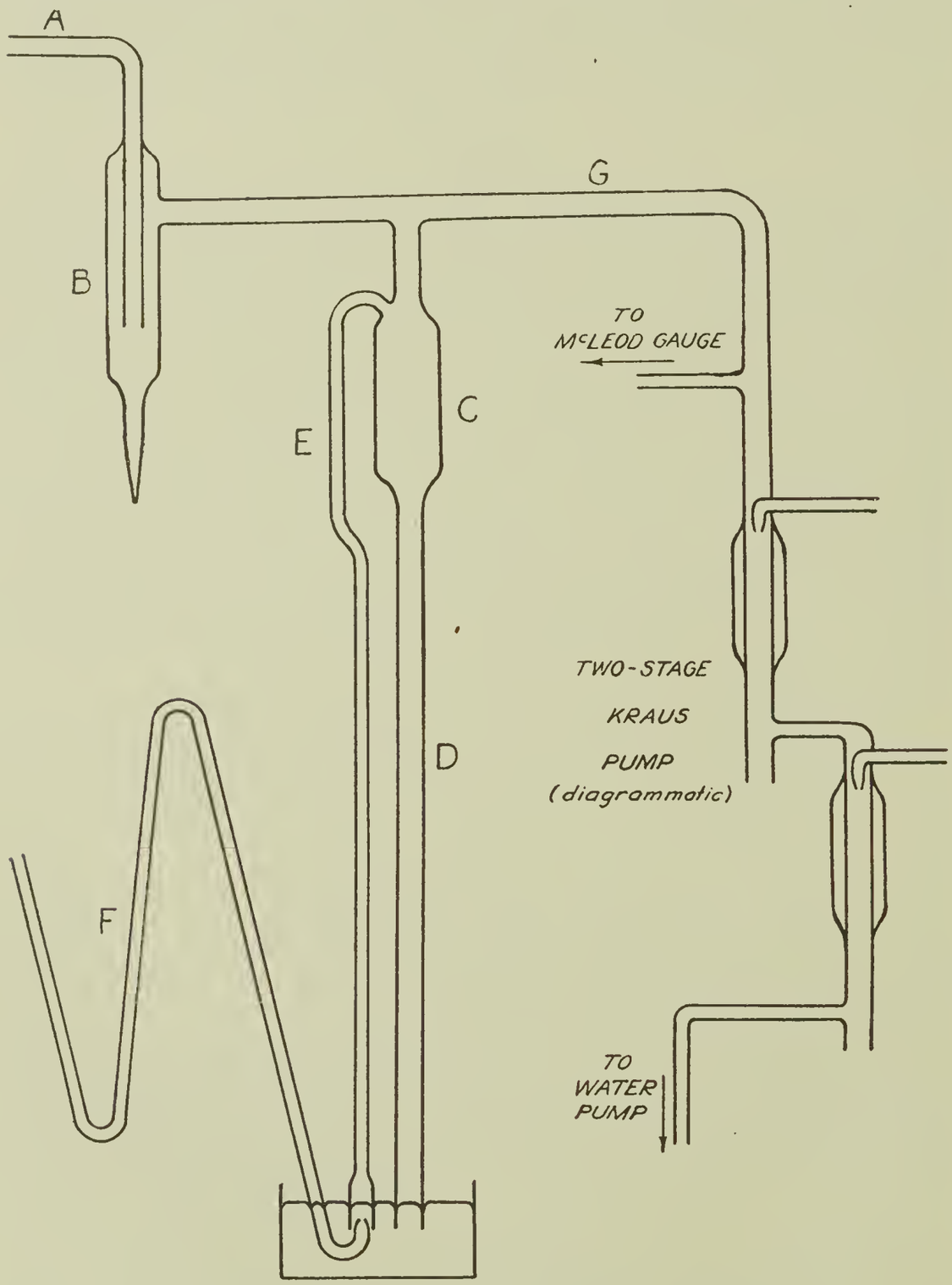


Fig. 3. Apparatus for supplying hydrogen to furnace.

reached in the present experiments, for a period of two hours, instead of for only two minutes, as was actually done. Examination of many of the alloys cast, confirmed these data, for no trace

of carbide could be found in any instance, despite the very sensitive test for its presence which is afforded by the evolution of hydrocarbons upon contact with moisture.

The soot, which was highly effective in preventing adherence of the cast rod to the mould, itself adhered loosely to the rod when the latter was withdrawn; but a brisk scouring with a stiff brush and some ligroine removed all traces of carbon, leaving the surface of the rod bright and clean.

Neutral Atmosphere.

Because of the great volatility of magnesium the melting and casting of the alloys had to be conducted in an inert atmosphere. Upon practical considerations hydrogen was selected, although argon, by reason of its greater density, would doubtless have been much more effective in reducing volatilization.

The hydrogen employed was the commercial electrolytic gas, and was passed in succession over a glowing grid-work of platinum wire, and over phosphorus pentoxide, in order to remove admixtures of oxygen or moisture. A contrivance which was found very convenient both because it permitted the rapid introduction of hydrogen into the highly evacuated apparatus, and because it served later as a safety valve to prevent an increase of pressure within the furnace when the latter was heated, is shown in Fig. 3. The gas coming from the tube *F*, rises through the column of mercury in *E*, and the entrained mercury returns through *C* and *D* to the reservoir below. The trap *B*, also shown in Fig. 3, was interposed between the furnace and the remainder of the apparatus, and was cooled by a mixture of carbon dioxide and ether, in order to prevent access of mercury to the alloys.

Alloys Obtained.

The alloys cast were in the form of rods, usually from 13 to 20 cm. long, and having an average diameter of about 7 mm., with a slight taper from end to end. Owing to blowholes produced by magnesium vapor, and in part perhaps by hydrogen, they were somewhat porous, and hence unsuited for determinations of electrical resistivity, although well adapted to observations of thermoelectromotive force and of the temperature coefficient of resistivity.

They were shown, both by chemical analysis and by micro-

scopic examination, to be highly uniform in composition throughout. The conditions in this system are indeed peculiarly favorable to the avoidance of segregation, since the component metals differ only slightly in density, and the liquidus and solidus curves of the equilibrium diagram lie close together, within the range of composition here considered, from 31 to 51 weight per cent magnesium.

THE CONSTITUTION OF THE SYSTEM ALUMINUM-MAGNESIUM.

1. *Previous Work.*

Numerous investigations have been made upon the constitution of the aluminum-magnesium alloys. Boudouard[20] observed the cooling of a series of alloys and partially established the liquidus. Grube[21] made a study of the system by means of thermal analysis, but did little micrographical work. He gave one compound Al_3Mg_4, indicated by an open maximum in the equilibrium diagram. This compound, according to the diagram, formed an eutectic with Mg and a band of solid solution with Al, terminating in an eutectic. The various possibilities suggested by Grube for the construction of solidus and liquidus for this solid solution field need not be stated here, since subsequent work has given more information. Supplementary data on the system were obtained by Wilm,[22] Eger,[23] Schirmeister,[24] Vogel[25] and Merica.[26]

The most comprehensive work which has been done on the constitution of this system is that of Hanson and Gaylor,[27] who made thermal and micrographical studies of forty compositions. The aluminum used contained impurities totalling 0.46 per cent, and the magnesium 0.25 per cent. The alloys were prepared in alumina-washed fireclay crucibles, and a lid was used to prevent excessive burning. After the alloys had been prepared in this way, heating and cooling curves were taken under conditions

[20] O. Boudouard, C. r., **132**, 1326; **133**, 1003 (1901). Bull. soc. Chim., **27**, 5, 45 (1902).
[21] G. Grube, Zeitsch. anorg. Chem., **45**, 225 (1905).
[22] A. Wilm, Metallurgie, **8**, 225 (1911).
[23] G. Eger, Int. Zeitzsch. Metallographie, **4**, 29-128 (1913).
[24] H. Schirmeister, Metal u. Erz., **11**, 522-3 (1914).
[25] R. Vogel, Zs. anorg. Chem., **107**, 265-307 (1919).
[26] P. D. Merica, Met. and Chem. Eng., **19**, 135, 200, 329, 587 (1918). *Cf.* also, P. D. Merica, R. G. Waltenberg and J. R. Freeman, Jr., Bull. Am. Inst. Mining Met. Engrs., 1031-49 (1919); Bur. Stds. Sci. Paper No. 337, 105-19 (1919); also Bur. Stds. Circ. No. 76 (1919): "Aluminum and Its Light Alloys."
[27] D. Hanson and Marie Gaylor, J. Inst. Metals, **24**, 201 (1920).

similar to those obtaining during preparation. The alloys were subsequently examined micrographically and analyzed for magnesium only. The authors' own interpretation of the results is shown in Fig. 4.

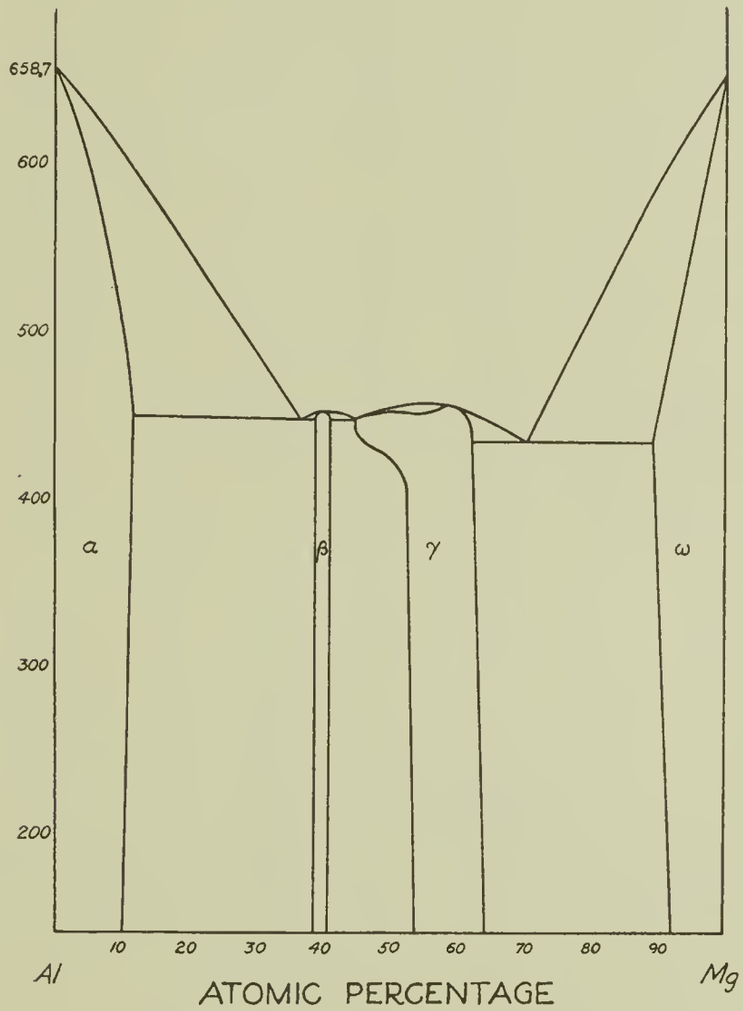


FIG. 4. Diagram of the aluminum-magnesium system.

The β-field with its compound Al_3Mg_2 had not been pointed out before, and the research established the slopes of the various lines with accuracy—remembering that thermal analysis and micrography alone were used. This is the most complete diagram which has been given for the system.

Comprehensive studies of conductivity were made by Pecheux[28] and also by Broniewski[29], whose results for conductivity and temperature coefficient of resistance are plotted in Fig. 5. Broniewski also made measurements on thermo-electromotive force. An

[28] H. Pecheux, Rev. gen. sci., **18**, 109-14 (1907).
[29] W. Broniewski, Compt. rend., **152**, 85-7 (1911).
Ann. chim. phys. (8), **25**, 1 (1912).

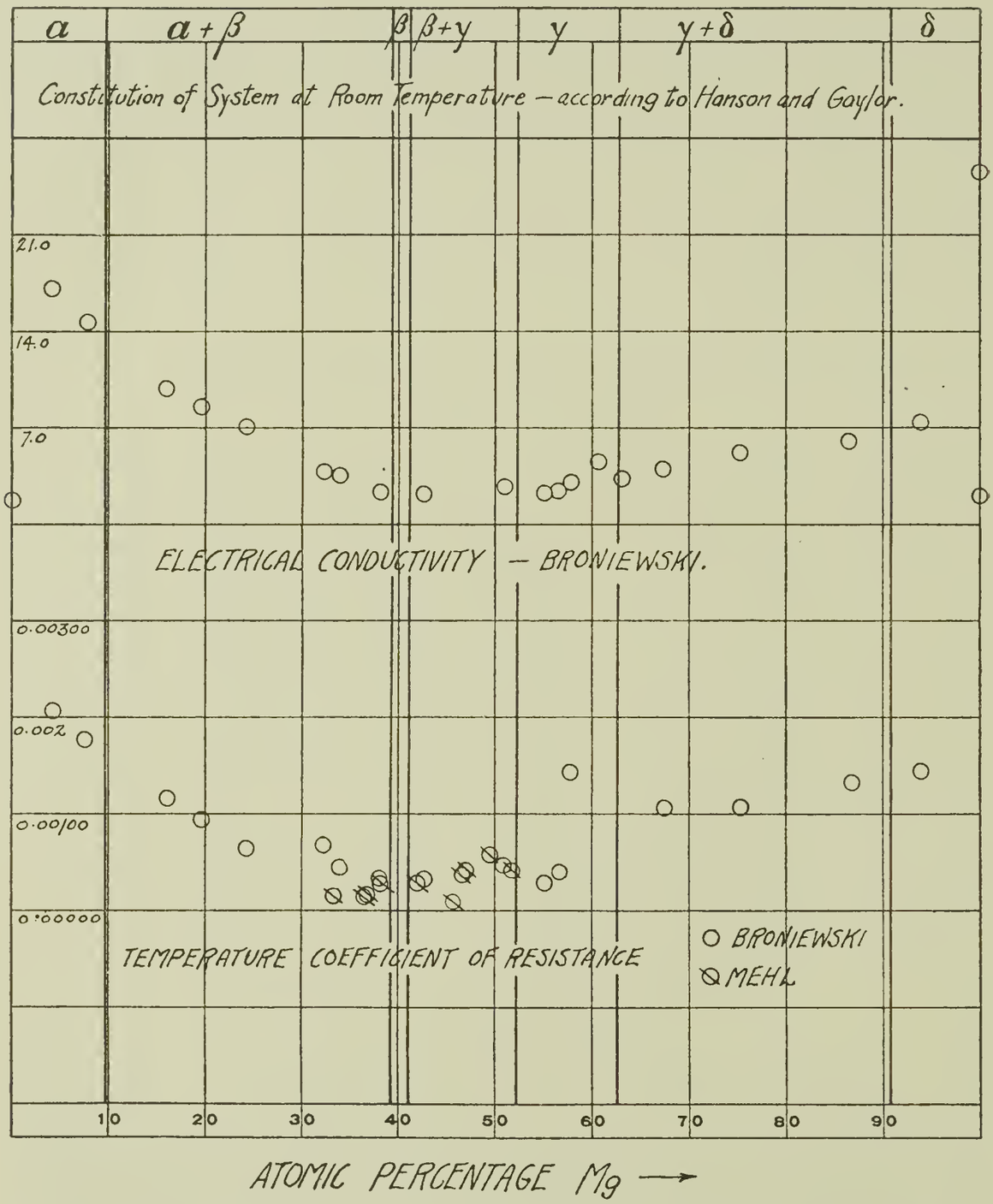


FIG. 5. Conductivity and temperature coefficient of resistance of the Al-Mg system.

earlier study of thermo-electromotive force was also due to Pecheux.[30] Northrup[31] reported a few observations upon conductivity, but the results are not given in such form that they can be compared with those of the other observers.

B. Ohtani[32] investigated a series of seven alloys ranging in

[30] H. Pecheux, Compt. rend., **139**, 1202-4 (1904).

[31] E. F. Northrup, Met. and Chem. Eng., **15**, 193-7 (1916).

[32] B. Ohtani, J. Chem. Ind., Japan, **25**, 36-52 (1922). (Quotations from this paper are from a translation made by Dr. S. Tashiro, of the staff of Chemical Abstracts.)

composition from 0–40 per cent Mg, by the method of thermal analysis, micrography, electrical resistance, tensile strength, hardness and specific gravity. The aluminum used contained 0.29 per cent Si, 0.14 per cent Fe, 0.04 per cent Cu, and the magnesium, 0.47 per cent Si, 0.02 per cent Fe. The alloys were prepared in a clay crucible and protected from atmospheric contamination by a flux of KNO_3-$NaNO_3$. During thermal analysis the alloys were covered with Mg powder in order to minimize burning with resulting change in composition. The equilibrium diagram proposed is similar to that of Hanson and Gaylor. The limit of the α-solid solution field was determined by measurements of electrical resistance at 320° and 400°; 7.3 per cent Mg is soluble in Al at 320°; 9.7 per cent at 400°. These figures indicate a solid solubility of Mg in Al lower than that proposed by Hanson and Gaylor. Ohtani observed the formation of a single phase in the neighborhood of 36 per cent Mg, corresponding to the β-field in Fig. 4, but did not show the presence of an open maximum on the liquidus in this range of composition. Ohtani's figures on electrical resistance, for some unknown reason, cannot be calculated into reasonable values for conductivity.

There are no measurements on electrical conductivity or thermo-electromotive force for alloys the compositions of which would place them in the β-field (Fig. 4). The results of Pecheux and of Broniewski show distinctly the presence of the compound Al_2Mg_3 in the γ-field (60 atomic per cent) and Broniewski's figures for conductivity and the temperature coefficient of electrical resistance contain measurements on a single composition in the $\beta + \gamma$-field which do not fall in line with those of the neighboring compositions (Fig. 5). This would indicate a greater complexity than that of a simple heterogeneous field. The measurements on thermo-electromotive force (Broniewski) show the presence of the compound Al_2Mg_3 and show a critical composition at 50 atomic per cent Mg corresponding to the limit of solubility of the γ-field.

Apparently neither Pecheux nor Broniewski paid particular attention to the purity of the alloys measured, for information on this point is very scanty in the papers of both.

2. *Present Work.*

Plan of Work.

Electrical data: Electrical conductivity, thermo-electromotive force and their temperature coefficients, for alloys of compositions between 32 and 52 atomic per cent Mg seemed desirable, inasmuch as such data would clear up the uncertainty in regard to the $\beta + \gamma$-field, would give electrical data on the β-field, and would fix the limit of solid solubility of the γ-field. The work about to be described affords data on the first and last of these points of inquiry.

A number of alloy rods of various compositions between 32 and 52 atomic per cent magnesium were prepared by the method already described in detail. Owing to volatilization, the composition of an alloy found by analysis was always about two per cent lower in magnesium than the synthetic composition. The use of argon as an inert atmosphere instead of hydrogen would no doubt diminish this loss to a large extent.

Properties of the Prepared Alloys.

The compositions of the alloys investigated were determined by analysis and are given in Table I. Analysis of various portions of an alloy rod showed the composition to be constant throughout to less than 0.1 per cent Al.

The silicon content of a typical alloy (50 per cent Al) was 0.026 per cent. This impurity doubtless originated in the starting material since the aluminum used contained a small amount. These figures indicate that no appreciable amount of silicon was introduced into the alloy during melting, and show definitely the value of the magnesia crucible.

Colorimetric tests with sulfocyanate failed to reveal the presence of any traces of iron, and it therefore appears that the lampblack coating on the casting tube supplied ample protection against contamination from this source.

The small amount of silicon was apparently the only impurity present in the alloy. The odor of hydrocarbon noticeable upon fracture of the magnesium could not be obtained from the finished alloy.

The alloy rods had diameters somewhat less than 6 mm. and lengths between 125 and 200 mm. They were smooth and regular

for 50 mm. from the bottom end, but for the rest of their length were uneven and constricted at various places. Most of the alloys were porous, containing blowholes which were doubtless caused by magnesium vapor.

The smoothness of the lower end of the rod indicated that a warm mould (casting tube) is necessary for the casting of sound alloys. The lower end of the rod was formed in the lower end of the casting tube which had remained in the melt for two minutes previous to casting and was therefore much warmer than the rest of the casting tube.

These rods, because of their unevenness and porosity, were unsuited for the measurement of electrical conductivity but were satisfactory for the measurement of the temperature coefficient of electrical resistance and of thermo-electromotive force and its temperature coefficient. They exhibited the marked brittleness which has been noted by all previous investigators of this system, and hence required very careful handling.

For the purpose of annealing, the alloy rods were sealed in sets of eight in evacuated glass tubes, which were heated for fifteen hours in the vapor of boiling diphenylamine (b. p. 308°). No volatilization of the magnesium was noted during this treatment, so that any change in composition was extremely small.

Measurement of Temperature Coefficient of Resistance.

In order to determine the temperature coefficient, the electrical resistance of each rod was measured at 25° ± 0.01° C. and again at a temperature near 100°. For the maintenance of the lower temperature an electrically heated and controlled thirty-liter oil bath was employed which had been in use for some years, and which can be depended upon to remain within the limits indicated. For the higher temperature, a smaller oil bath of similar construction was used, which is designed to maintain a temperature of 100°. As this thermostat was still, however, in process of development, and the automatic control permitted slow fluctuations of several degrees, the actual temperature was found for each observation of resistance. For this purpose a certified quartz thermometer served, the scale of which is divided to degrees.

The making of satisfactory contact with the alloy rods proved to be a matter of much difficulty. The customary method of

making the potential-point contacts of the Kelvin bridge connection by means of screw clamps provided with knife edges or needle points was not feasible, owing to the extreme brittleness of the alloys, in consequence of which light-pressure contacts failed to hold, and heavy-pressure contacts caused fracture of the rods. The plan finally adopted was to electroplate four narrow zones of each rod with copper, and to solder the leads to this copper. Paraffin was used to "stop off" the portions of the rod upon which plating was not desired, and the copper was deposited from an alkaline cyanide solution, since acid solutions attack the alloys. This method gives a good electrical connection, but it possesses the disadvantage that local heating during soldering may render the alloy physically inhomogeneous, and hence affect its resistance. Since the soldering was done with care to avoid any greater heat than was necessary, it is not likely that serious error was thus introduced.

TABLE I.

Temperature Coefficient of Resistance.

Composition of Rod		Resistance at 25° C x 20	Resistance at high temperature x 20	Temp. Coeff. $\alpha \times 10^4$
Weight per cent Mg	Atomic per cent Mg			
31.00	33.28	0.02453	0.02481 at 100.9°	1.411
34.13	36.52	0.01662	0.01692 at 100.0°	1.353
34.48	36.88	0.02788	0.02822 at 98.8°	1.648
35.92	38.40	0.01832	0.01873 at 100.0°	2.984
39.54	42.07	0.02322	0.02371 at 98.8°	2.800
43.30	45.88	0.01581	0.01591 at 99.8°	0.846
44.24	46.84	0.01041	0.01070 at 100.5°	3.690
44.48	47.08	0.04914	0.05071 at 100.3°	4.243
47.12	49.72	0.01223	0.01276 at 100.3°	5.755
50.25	52.85	0.02527	0.02607 at 99.9°	4.202

Measurements were made by first placing the rod with its connections in the 25° thermostat, noting the reading after a constant value for the resistance was reached, then repeating the process in the 100° bath and returning the rod to the first bath for a final check. The Kelvin double-bridge used reads to two ohms in steps of 0.0000005 ohm, with an accuracy of 0.1 per cent.

The galvanometer is of the Broca type, protected by a proportional shunt.

The results of these measurements are summed up in Table I and are given graphically in Fig. 5. As can be seen from the table and graph, the results of the measurements were such that they can be regarded only as preliminary. With the exception of a single composition, 43.30 weight per cent magnesium, the values rise fairly steadily as the percentage of magnesium increases, as might be expected in a heterogeneous field. There are no values indicating the presence of a compound or of a solid solution field. None of the compositions fell within the composition range for the β-field indicated by Hanson and Gaylor, and the measurements do not throw any light upon the question as to the existence of this field.

Measurement of Thermo-Electromotive Force.

The thermo-electromotive forces of the alloys were observed against annealed copper. The making of satisfactory contacts was a simple matter in this case. The ends of the rod to be measured were well cleaned to expose a fresh surface, and connection was made to them by means of a thin strip of lead foil, wired tightly to the rod. The copper connecting wire was imbedded in an overlapping end of the lead strip.

During the measurement the rod was in an upright position. The upper end of the rod entered a small cup in which was kept an ice-water mixture which served to keep the cold junction at 0° C. The glass cup was well insulated by felt and during the measurement fresh ice was constantly, although slowly, fed into the cup, and the excess of water pipetted off. A single wire of annealed copper was connected to this end of the rod.

The lower end of the rod dipped into a high-boiling oil, contained in a beaker of such capacity that the bath, after being heated to somewhat above the temperature desired, cooled very slowly during the course of an experiment. One junction of a copper-constantan thermo-couple served for the electrical connection to this end of the rod. Thermal insulation between the beaker and the ice bath was provided by several layers of thick felt, placed upon asbestos-board screens.

A Leeds & Northrup potentiometer, type K, was used here,

together with the Broca galvanometer mentioned in the preceding section.

The copper-constantan thermo-couple for the measurement of the temperature of the hot junction was calibrated at the boiling points of water and naphthalene, corrected for barometric pressure, and at the freezing point of tin. The cold junction was kept at 0° C. by means of ice and water in a Dewar flask.

The calibration figures are as follows:

Temperature ° C.	E. M. F.
99.93	0.004115
217.87	0.009840
231.9	0.010588

These figures give points all of which fall accurately upon a parabolic curve of electromotive force against temperature. The equation for the couple, constantan against copper, was as follows, accurate to the fourth figure:

$$E.\ M.\ F. = -\ 0.00003779\,t\ -\ 0.00000003385\,t^2$$

The approximate temperature of the oil bath was read on an ordinary thermometer. When the thermometer showed a temperature in the neighborhood of 100°, the copper-constantan thermo-couple was connected to the potentiometer, two successive voltages read off and the time of each reading noted. Then the thermo-couple lead wire was quickly disconnected and the other copper wire, joined to the other end of the rod, was connected to the potentiometer and the thermo-electromotive force of the alloy rod couple was read and the time noted. This copper wire was removed as quickly as possible and the original wire replaced, and two successive voltages were noted together with the respective times. These operations were repeated in the neighborhood of 75°. The two sets of observations, therefore, gave data from which the thermo-electromotive force of the alloy rod could be graphically determined for two temperatures.

The figures recorded in Table II, obtained from actual measurements, are typical.

The particular voltage of the copper-constantan couple corresponding to the time at which the reading on the alloy-rod couple was made can be obtained graphically from the times given in the first column. This voltage can be transformed to degrees by

substituting in the equation for the copper-constantan couple given above. Thus, the first measurement gives 0.003658 volt for the alloy-rod couple at a temperature of 103.60°, while the second measurement gives 0.002391 volt at a temperature of 69.91°.

TABLE II.

Thermo-electromotive Force. Alloy 48.2 Per Cent Mg by Weight.

Time	E. M. F. from temp. couple	E. M. F. from alloy-rod-couple
38.09	0.004348	
38.35	0.004318	
39.14		0.003658
40.07	0.004227	
40.40	0.004198	
14.00	0.002799	
14.29	0.002782	
15.08		0.002391
15.57	0.002744	
16.32	0.002729	

From these values, the equation for the alloy-rod couple, alloy against copper, can be obtained:

$$\text{E. M. F.} = -\ 0.00003191\ t - 0.00000003289\ t^2$$

In this way an equation for each rod was obtained, and comparison between the rods was made by substituting 100 for *t* in each case, which gave values for the thermo-electromotive force at 100°.

The first differential of the equation gives a form:

$$\frac{dE}{dt} = -\ 0.00003191 - 0.00000006578\ t$$

from which the "thermo-electric power" at 100° can be calculated, when 100 is substituted for *t*. This quantity also served as a basis of comparison.

The equations for the various alloy compositions, giving the E. M. F. as a function of temperature, appear in Table III.

The curves for this series of alloys of thermo-electromotive force and "thermo-electric power" are given in Fig. 6, which gives the values of these two functions referred to lead. Each of these values may be obtained by combining the equation in

Table III with Broniewski's equations for copper against lead, in microvolts,

$$\frac{dE}{dt} = 2.88 + 0.0098\,t,$$

which gives an equation for the alloy against lead, and then substituting 100 for *t* in this equation.

TABLE III.

Thermo-electromotive Force Al-Mg Alloys.

Composition of Alloy		Equation for Thermo-Electromotive Force, E, in volts
Weight per cent Mg	Atomic per cent Mg	
31.00	33.28	$E = -0.0_{4}3442\ t - 0.0_{7}2787\ t^2$
34.13	36.52	$E = -0.0_{4}3778\ t + 0.0_{8}8781\ t^2$
34.48	36.88	$E = -0.0_{4}3459\ t - 0.0_{7}2429\ t^2$
35.92	38.40	$E = -0.0_{4}3367\ t - 0.0_{7}2665\ t^2$
39.54	42.07	$E = -0.0_{4}3580\ t - 0.0_{8}2823\ t^2$
43.30	45.88	$E = -0.0_{4}3861\ t + 0.0_{7}1243\ t^2$
44.24	46.84	$E = -0.0_{4}3365\ t - 0.0_{7}2448\ t^2$
44.48	47.08	$E = -0.0_{4}3293\ t - 0.0_{7}2079\ t^2$
47.12	49.72	$E = -0.0_{4}3337\ t - 0.0_{7}2065\ t^2$
48.20	50.80	$E = -0.0_{4}3191\ t - 0.0_{7}3289\ t^2$
49.12	51.74	$E = -0.0_{4}3459\ t - 0.0_{7}1490\ t^2$
50.25	52.85	$E = -0.0_{4}7892\ t + 0.0_{6}1668\ t^2$

The curves in Fig. 6 show very clearly the linear relations between the two functions, thermo-electromotive force and "thermo-electric power," and composition up to 50.25 weight per cent magnesium, and accord with the probability that the system within the range of composition from 31.00 to 49.12 weight per cent magnesium is of a heterogeneous nature—with the possible exception of the β-field.

The limiting concentration of the γ-field is very decidedly shown by the sudden decrease in E_{100} at the composition 50.25 Mg. The limit of solid solubility appears to lie between 51.74 and 52.85 atomic per cent Mg and is placed arbitrarily at 52.30 atomic per cent Mg, which is 49.80 weight per cent. Hanson and Gaylor gave 54 atomic per cent Mg or 51.30 weight per cent, as the limit of the field.

The agreement between the results obtained in this work and

the constitutional diagrams proposed for the Al-Mg system has been discussed completely in the preceding paragraphs; and the information which these results have furnished as regards con-

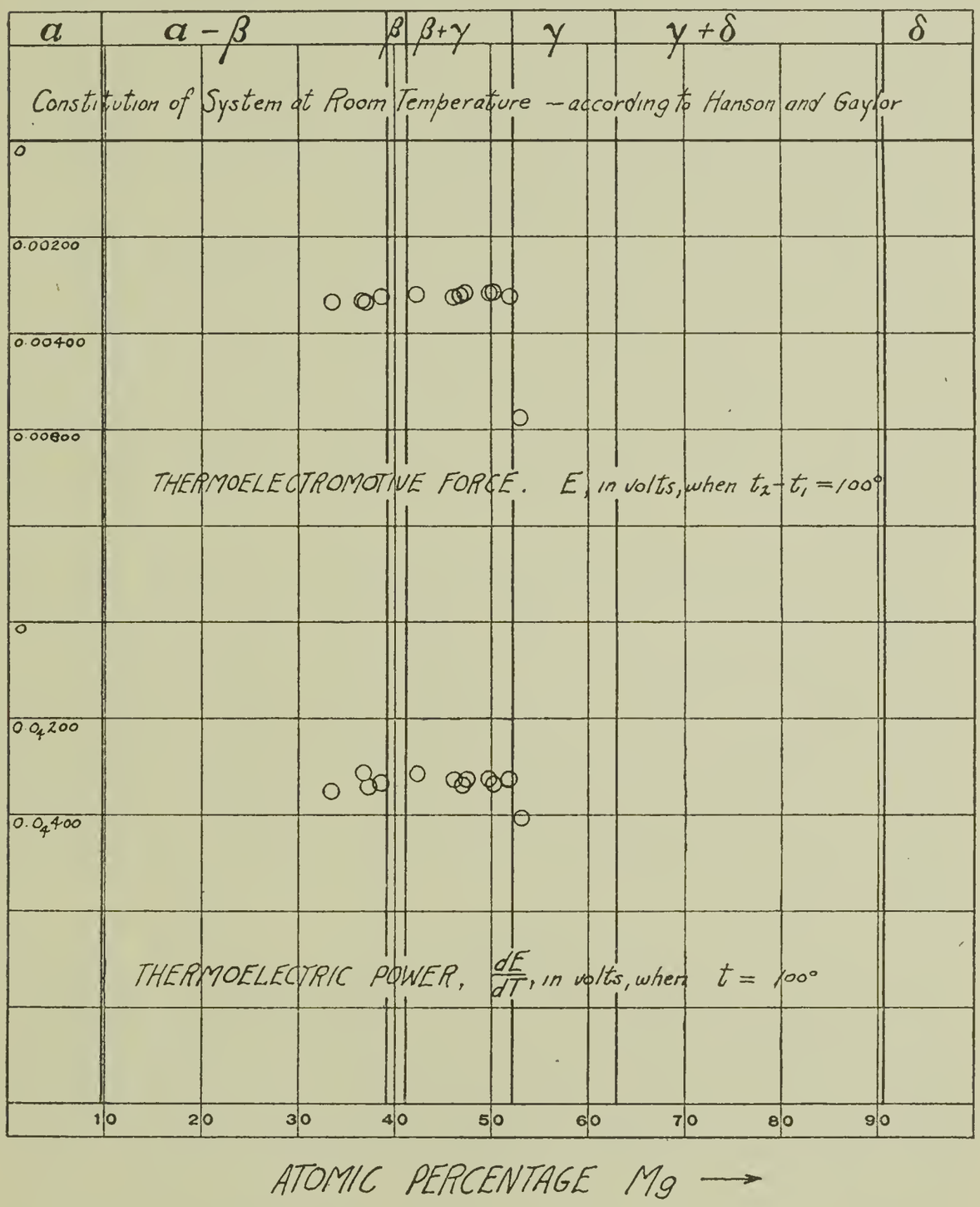


FIG. 6. Thermo-electromotive force and thermo-electric power, Al-Mg alloys.

stitution has been compared to that obtained by other investigators working along similar lines. It remains to point out the relation between the values obtained here for the electrical properties and those obtained by the other workers.

Broniewski's measurements[29] upon alloys of compositions between 32 and 51 weight per cent magnesium give values for the temperature coefficient of resistance, α, varying irregularly from 0.00060 at 32 per cent Mg to 0.00030 at 51 per cent. The results obtained in this work are lower and the value for α increases with increasing magnesium content from 0.00014 to 0.00042. Pecheux's[30] results for conductivity and temperature coefficient of resistance are not given here because of the very large amount of impurity present in the alloys measured.

Pecheux[28] also measured the thermo-electromotive force of these alloys against copper and found a value of 128.69 microvolts for an alloy containing 34 per cent Mg. These alloys, however, also contained considerable impurity, affecting the thermo-electromotive force to an unknown but certainly very considerable degree. The same statement is valid with regard to the work of Broniewski, whose alloys contained about 1 per cent impurity.

A typical alloy, 31 per cent Mg, referred to Pb, gives a value for E_{100} of — 33.34 microvolts, while Broniewski's figures for an alloy containing 30 per cent Mg give a value of — 0.97. Broniewski's alloys showed a gradually decreasing thermo-electromotive force with increasing magnesium content up to 45 per cent Mg where a very abrupt decrease took place, the value reaching — 4.20 microvolts at about 48 per cent Mg. The curves on Fig. 6 show a similar rapid decrease between the composition 49.12 and 50.25.

SUMMARY.

Briefly, the electrical data here presented give information on two points in connection with the system aluminum-magnesium; they confirm the heterogeneous nature of the $\beta + \gamma$-field of Hanson and Gaylor, and fix the limit of the γ-solid solution field at 52.30 atomic per cent Mg, or 49.80 weight per cent.

DISCUSSION.

Fulton B. Flick[33]: Mr. Mehl's work on the preparation of pure magnesia crucibles is very interesting and is certainly valu-

[33] Metallurgist, Res. Bureau, Aluminum Co. of America, New Kensington, Pa.

able, in that it gives promise of providing a more satisfactory container for the preparation of certain types of alloy systems containing a minimum of impurities. With reference to the casting difficulties mentioned on page 163, namely, porosity, it would seem that the selection of hydrogen for the inert gas was somewhat unfortunate. As is well known, hydrogen is readily soluble in many metals, and under the conditions which he worked, the molten alloy would be saturated with hydrogen. When the pressure was reduced in order to draw the alloy up into the tube, the hydrogen would, of course, tend to come out, and it is highly probable that the difficulties were due more to this factor than to the factors mentioned in the paper. In the work of the Japanese investigator, Ohtani, referred to on page 167, it is rather startling to read that in order to prevent burning of the alloys he covered them with powdered magnesium. It seems likely that an error was perhaps made in translating the paper, and that powdered magnesia (MgO) was really meant, which might be satisfactory under the circumstances. At any rate, it would not offer the danger that powdered magnesium would. With reference to the solubilities given on page 167, the equilibrium diagram of Hanson and Gaylor for aluminum-magnesium, indicates a solubility of approximately 10 per cent aluminum in magnesium at 435°. As stated in the magnesium handbook, published by the American Magnesium Corporation, some work which was done in the laboratories of the Aluminum Company of America indicated a somewhat greater solubility than this and also that the solubility decreases somewhat more rapidly with falling temperature than is indicated in the diagram referred to. With reference to the analysis of the alloys I wish to speak of the silicon content of the 50-50 alloy. The aluminum used in making this alloy is reported to have contained 0.15 per cent silicon. The alloy should, therefore, have analyzed about 0.075 per cent silicon, instead of 0.026 per cent, as reported. Such material reduction of the silicon content is unlikely. The same applies to the iron content of the same alloy. It is stated that, "colorimetric tests with sulfocyanate failed to reveal any traces of iron . . . ." Yet this same alloy should contain approximately 0.09 per cent iron. Much lower iron contents are commonly determined with high precision in the laboratories of the Aluminum Company of America, by titration with potassium

permanganate. However, since this procedure (sulfocyanate) is known to be a very delicate test for iron, providing the iron is in the ferric state, I should like to ask Mr. Mehl if he took precautions to insure this before adding the reagent. Naturally, in dissolving such an alloy any iron present will be in a ferrous condition.

B. Ohtani[34] (*Communicated*): The work of Dr. R. F. Mehl deserves our full admiration. I should like to point out two or three errors in the text, page 167, referring to my experiments. I made up a series of magnesium alloys and used a clay crucible in some cases, and in other cases a magnesia crucible. During thermoanalysis, the alloys were covered with magnesium oxide powder, not magnesium powder. On the annealing of the samples, a potassium nitrate-sodium nitrate salt bath was used, in order to avoid change in composition. Referring to my figures on electrical resistance, these do not designate the specific resistance, but the resistance of specimens, 5 mm. in diameter and 70 mm. long, which had been made from chilled cast ingots and had been annealed at different temperatures. It is to be noted that these values when reduced to specific resistance give values of reasonable magnitude.

Robert Franklin Mehl (*Communicated*): Mr. Flick's comment on the use of hydrogen as an atmosphere, during the preparation and casting of the alloys, touches upon one of the chief experimental difficulties encountered in this work. Early experiments on the preparation of Al-Mg alloys *in vacuo* demonstrated conclusively the impossibility of controlling the volatility of the Mg, and the problem resolved itself into the choice of an inert gas. The gases helium, neon and argon would be most suitable in preventing volatilization, the efficiency of the gas in this respect presumably increasing with increase in density. After some experiments with a small quantity of very pure argon, kindly supplied by Mr. Holderer, of the Air Reduction Sales Company, it became evident that a gas available in greater quantity would be necessary with the apparatus used, since each run consumed about three liters. Recovery of the gas after each run and its purification would have entailed a great deal of labor and expense. The

[34] Imperial University, Sendai, Japan.

availability of cheap helium, neon or argon for the preparation of pure alloys is much to be desired.

Hydrogen was therefore chosen, though its use carried with it several disadvantages. The solubility of hydrogen in the Al-Mg alloys, as Mr. Flick points out, was doubtless the cause (in part) for the porosity of the cast alloys. There seems to be no data on the solubility of hydrogen in molten Al-Mg alloys, though it has been known for some time that molten aluminum dissolves considerable amounts.[35] On the other hand the hydrogen probably reduced the amount of oxygen introduced into the atmosphere from the apparatus during the preparation of the alloys, and therefore to some extent prevented oxidation. This is an important advantage for it was found that a very small amount of oxidation caused the Al and Mg particles to be coated with a thin film of oxide, which parially prevented their alloying.

The analysis of the aluminum, given on page 159, is one taken from the Bureau of Standards Circular No. 66, and gives the average amount of impurity present. In the present work the starting material was not analyzed, but the finished alloys were tested for the elements reported in the analysis, and for those that might have been introduced during the preparation of the alloy. Any discrepancy beween the Bureau of Standards analysis and the ones obtained for the finished alloys was doubtless due to the fact that the starting material contained less than the average impurity, and that perhaps some "clean-up" occurred during the preparation of the alloys.

The sulfocyanate test for iron was carried out after oxidation with nitric acid. The red color produced by the action of the excess nitric acid upon the sulfocyanate reagent was destroyed by heating.

It is unfortunate that Professor Ohtani's valuable paper had to be read through the medium of the work of a translator, since, evidently, several errors have crept into the work due to errors in the translated copy. I am glad to have Professor Ohtani's correction of these. "Magnesium" on page 167 should be "magnesium oxide." With respect to the figure for electrical conductivity, the "unknown reason" mentioned on page 167, in the light of Professor Ohtani's communication, was the substitution in the

[35] M. Guichard and P. Roger-Jourdain, Bull. Soc. Chim., 11, 421 (1912).

translated copy of "cm." for "mm." With this correction the value for the resistivity of Professor Ohtani's Al (Al = 99.53; Si = 0.29; Fe = 0.14; Cu = 0.04) calculates to 3.001×10^{-6} ohms for the centimeter cube (temperature not stated), and this figure compares favorably with the Bureau of Standards figure, 2.828×10^{-6} at 20° for commercial aluminum (Al = 99.57; Si = 0.29; Fe = 0.14). The difference between these two figures may have been due in part to the greater impurity (Cu = 0.04) in Professor Ohtani's aluminum, and perhaps in part to a higher temperature of measurement.

A paper presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 4, 1924, President Parmelee in the Chair.

THE PREPARATION OF METALLIC TUNGSTEN AND SOME OF ITS ALLOYS.[1]

By Louis Kahlenberg and Herman H. Kahlenberg.[2]

Abstract.

Tungstic acid, H_2WO_4, and tungstic acid anhydride, WO_3, are soluble in fused alkali halides, and from such fusions alkali tungstates, metallic tungsten, tungsten bronzes, and tungsten alloys may be prepared. When WO_3 is added to fused sodium chloride, chlorine is liberated and a compound $Na_2O.W_2O_5$ is formed, which dissolves in the excess of NaCl present. When H_2WO_4 is added to fused NaCl, HCl is liberated and alkali tungstates are formed. It requires prolonged heating to expel the last traces of HCl from such fusions. A smooth deposit of exceedingly pure and very ductile metallic tungsten was obtained from the proper fusions by electrolysis, using low current densities and low voltages. At higher current densities, the metal separates out in granular or pulverulent form. From fusions very rich in tungsten, tungsten bronzes are deposited on the cathode. This is a new method of preparing such bronzes. Tungsten was also prepared from the fusions by chemical displacement with other metals. According to these replacement experiments, the position of tungsten in the electrochemical series lies betwen zinc and iron. Various tungsten alloys were prepared by new methods.

Since Scheele's researches on tungsten in 1781, many methods of preparing metallic tungsten have been devised. These have been sufficiently described by Mennicke in his book on "Die Metallurgie des Wolframs," so that they need not be detailed here.

[1] Manuscript received July 14, 1924.

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In 1924 Mann and Halvorsen[3] attempted to electroplate tungsten on iron. They did not succeed in getting a metallic deposit except when they used fused lithium chloride as an electrolyte. A tungsten anode and an iron cathode were employed. They obtained a thin metallic deposit on the cathode, which, however, probably consisted of iron and tungsten, since their tests showed iron to be present in the electrolyte, and it is well known that iron is more readily deposited than tungsten.

The fact that their deposit was not attacked by concentrated hydrochloric acid, does not necessarily show that the deposit was free from iron. Indeed, such a deposit might contain relatively large amounts of iron and yet not be attacked by concentrated hydrochloric acid. (Compare, for example, Mennicke, p. 269, on W_2Fe_3.) Moreover, Mennicke, p. 198, shows that metallic tungsten deposits have been obtained by electrolysis of fusions of sodium chloride and tungsten chlorides using tungsten electrodes, so that the observation of Mann and Halvorsen using LiCl instead of NaCl really presents nothing new in principle.

EXPERIMENTAL.

The present research is based upon the new discovery that tungsten trioxide and tungstic acid are soluble in fused alkali chlorides,[4] and that from such fusions metallic tungsten and also alloys of tungsten may be prepared by electrolysis. While the electrolytic deposition of tungsten was originally the chief aim, the investigation led to the preparation of tungsten and some of its alloys by chemical replacement methods which are quite new.

I. THE REACTION OF WO_3 AND H_2WO_4 ON MOLTEN NaCl.

As already stated above, it was found that tungstic acid is soluble in molten alkali chlorides, of which, of course, common salt is the cheapest, and so the first step was to investigate the extent of this solubility. For this purpose very pure tungstic acid was carefully dehydrated by heating it to a red heat for five hours. One hundred grams of sodium chloride was fused in a porcelain crucible, and then the anhydrous WO_3 was added in small amounts till the solution was just saturated. It required

[3] Trans. Am. Electrochem. Soc., 45, 493 (1924).

[4] Also in other alkali halides.

21.3 grams of WO_3 to accomplish this, as was readily determined by adding the WO_3 to the fusion till a visible trace remained undissolved. This proportion corresponds approximately to 1 gram molecule of WO_3 to 20 gram molecules of NaCl. Chlorine gas was evolved during the process of dissolving the WO_3 in the molten NaCl, showing that a chemical reaction was taking place. The fusion was cooled and extracted with water. Most of the mass dissolved readily, but a small amount of white powder remained insoluble. The latter, on treatment with hydrochloric acid, yielded WO_3 and NaCl, showing that it was one of the insoluble tungstates. It was not investigated further.

A similar fusion was now made and the loss in weight due to the evolution of chlorine was determined. The loss in weight was found to be 40 grams per gram-molecule of WO_3 dissolved. A blank fusion containing Na_2WO_4 and NaCl was run under identical conditions, and the loss due to volatilization was found to be four grams. This yielded the corrected value of 36 grams of chlorine evolved for every gram-molecule of WO_3 dissolved. These quantitative data may therefore be represented by means of the following equation:

$$2WO_3 + 2NaCl = Na_2O.W_2O_5 + Cl_2$$

There is indeed a tungsten "bronze"* of this composition $Na_2O.W_2O_5$, or $Na_2W_2O_6$, known. This compound was prepared, and it was found to be soluble in molten NaCl. The fusion or treatment with water yielded an alkaline reaction and an insoluble residue, a behavior which is precisely like that observed when the fused mass of NaCl and WO_3 is treated with water.

The solubility of H_2WO_4, or hydrated WO_3, in fused NaCl was also determined. It was found that 560 grams of H_2WO_4 dissolved in 58.5 grams of molten common salt. Large amounts of hydrochloric acid gas were evolved during the process of solution. The result corresponds to 510 grams of WO_3 per gram molecule of NaCl, or between four and five mols of WO_3 to every two mols of NaCl. Since HCl was evolved during the reaction the compound formed was probably an acid tungstate of the formula $Na_2O.4WO_3$ or $Na_2O.5WO_3$. The fusion was homo-

* The term "bronze" is here used to mean a metal or metal compound powder usually brought into suspension in amylacetate and applied to the surface of steam radiators and the like.

geneous, contained no chlorides and was completely insoluble in water. Its properties indicated it to be the compound $Na_2O.5WO_3$ described by Mennicke.[5]

I. PREPARATION OF TUNGSTEN BY ELECTROLYSIS.

In order to depress the melting point of the fusions a mixture of NaCl and KCl, instead of pure NaCl, was used in the following experiments:

Fifty grams of NaCl and 10 grams of KCl were fused in a porcelain crucible. Sixty grams of H_2WO_4 were gradually added. As this dissolved, large quantities of HCl gas were evolved. Carbon electrodes were placed into the fused mass and the electrolysis was started, using 5 volts and a current density of 0.3 amp. per sq. cm. Oxygen was rapidly evolved at the anode and a large cluster of lustrous red and blue needles was deposited at the cathode. These needles were found to be alkali tungsten "bronzes," consisting of a compound of Na_2O or K_2O with a low oxide of tungsten. They had all the properties of such compounds as described by Mennicke in his treatise.

A fusion consisting of 50 grams of NaCl, 50 grams of KCl and 50 grams of H_2WO_4 was electrolyzed, using a tungsten anode and a molten lead cathode. The anode was corroded and no gas was evolved. The e. m. f. was 4 volts and the current density 1 amp. per sq. cm. at the anode and 0.5 amp. per sq. cm. at the cathode. The temperature was about 800° C. The molten lead cathode gradually became more and more viscous until it finally solidified. It was then removed and analyzed and found to consist of 78.0 per cent lead and 21.9 per cent tungsten. Pure metallic tungsten was obtained from this alloy by dissolving the lead with dilute nitric acid and removing the small amount of WO_3 formed by the nitric acid, with ammonia. Quantitative analysis showed the product to be 100 per cent pure tungsten, within the limits of experimental error.

Carbon electrodes were used in the next electrolysis. A solution of 5 per cent of H_2WO_4 in a fusion of equal parts of NaCl and KCl was made. On electrolysis the carbon cathode was violently attacked, breaking into small pieces. This was apparently due to the deposition of metallic sodium, forming a carbide

[5] Die Metallurgie des Wolframs, p. 48.

which immediately decomposed, disintegrating the electrode. When a like fusion was electrolyzed with a carbon anode and a nickel cathode, a white precipitate was formed at the cathode, while oxygen was evolved at the anode. This precipitate was probably subchloride of sodium,[6] a compound which has also been observed by others when electrolyzing fused sodium chloride.

A fusion of equal parts of NaCl, KCl, and H_2WO_4 was electrolyzed between carbon electrodes, using a current density of 0.5 amp. per sq. cm. and a potential drop of 3 volts. The electrolysis was begun immediately after dissolving the H_2WO_4. A deposit of black powder and shining metallic curls was formed on the cathode. The deposit did not adhere well, but dropped off from the cathode, settling to the bottom of the porcelain crucible. The deposit was separated from the fusion by extraction with water. Analysis showed it to be 100 per cent pure tungsten. The little curls of metal obtained were thin and brittle, but had the steel-gray hue of pure tungsten metal.

A fusion of 50 grams NaCl and 50 grams KCl was made in a porcelain crucible. Twenty grams of H_2WO_4 was added to this and the fusion was then electrolyzed, using carbon electrodes. The e. m. f. was 5 volts and the current density 1 amp. per sq. cm. Tungstic acid was added from time to time to keep the tungsten content of the electrolyte approximately constant. Oxygen was evolved at the anode and tungsten was deposited in metallic curls. In this fusion 20 grams of H_2WO_4 was used to 100 grams of the NaCl-KCl mixture, while in the previous experiment 50 grams of H_2WO_4 were similarly employed. Nevertheless, in both experiments the electrolysis proceeded in precisely the same manner, that is to say, the products at the electrodes were identical in character. After the electrolysis had been run long enough to deposit 15 grams of metallic tungsten, the electrodes became short-circuited, due to the deposit floating off into the electrolyte. The heavy tungsten was carried in the convection currents. The current efficiency in this experiment was approximately 80 per cent.

Four additional experiments were conducted in a similar way. In these the electrolyte contained 10 grams, 20 grams, 30 grams and 40 grams of H_2WO_4, respectively, per 100 grams of the NaCl-KCl mixture. In all four of these cases a current efficiency

[6] Abegg Handbuch d. anorg. Chem., 2, 1, p. 221.

of only 80 to 85 per cent was obtained. This was due to partial short circuiting of the electrodes through the walls of the porcelain crucible, which proved to be an excellent conductor at the fusion temperature. By using a graphite crucible as cathode and as container, and a carbon anode suspended in it, a yield of 100 per cent was obtained.

The fact that tungsten could be deposited on a carbon electrode as a little curl suggested the possibility of making a smooth deposit of this metal from a similar fusion. With this idea in mind, a preliminary experiment was performed as follows: An unweighed portion of H_2WO_4 was added to a fusion of equal parts of NaCl and KCl. The amount of H_2WO_4 was roughly estimated to be about 20 grams to 100 grams of the NaCl-KCl mixture. A carbon anode and a nickel cathode were placed in the fusion and a current density of 0.015 amp. per sq. cm. was used. The drop in potential across the electrodes was 0.2 volt. The cathode remained clean in appearance and unattacked. After three hours, the cathode was removed and washed. It was found to be covered with a fine, even deposit of a steel gray metal.

Nitric acid was without action on this deposit, indicating that it was tungsten. As the deposit was rather thin, it could not be removed from the nickel cathode except by dissolving the nickel away with nitric acid. This was done, and there was left a thin sheet of steel gray metal which was exceedingly ductile, in fact, nearly as much so as a similar sheet of aluminum. The deposit was analyzed, the tungsten being weighed as WO_3. The metal was found to be 99.9 per cent pure tungsten.

The next step was to duplicate this experiment. This proved to be a most difficult thing to do. Thirty-two fusions were made, using as nearly as possible the same conditions, but every one of these fusions attacked the nickel cathode rapidly, and the only tungsten metal that could be deposited was in the form of a black powder. The fact that the nickel cathode was attacked was due to the presence of hydrochloric acid dissolved in the fusion. The nickel was dissolved as chloride, giving the fusion an intense blue color. This hydrochloric acid was formed by the action of the H_2WO_4 on the NaCl as already mentioned above, and it could not be driven off completely without heating the fusion at 800° C. for many hours.

The presence of hydrochloric acid in the fusion was proved conclusively by the fact that hydrogen was evolved in small amounts during the electrolysis. Even after heating a fusion for four hours at red heat hydrochloric acid could be detected in the vapors over the crucible. Even H_2WO_4, which had been heated for several hours at red heat, still evolved hydrochloric acid gas when added to fused sodium chloride. This shows that it is quite difficult to dehydrate H_2WO_4 completely.

As the customary method of analysis for tungsten is to weigh the latter as WO_3, great care must be used to obtain the latter in perfectly anhydrous condition, which requires many hours of heating. It was also observed that in these fusions the action of HCl was far more vigorous than in aqueous solution, which was to have been expected on account of the much higher temperatures of the fusions. As long as the fusion still contained hydrochloric acid, Ni, Co, Fe, Cu, or Ag would be rapidly dissolved by it without throwing out any tungsten. Cobalt, indeed, serves as an excellent indicator of the point when all HCl has been expelled, for as long as any of the latter gas remains, cobalt will dissolve, giving the fusion an intense blue color. When HCl has been volatilized, cobalt remains in the fusion quite unattacked.

If Na_2CO_3 is added to a fusion which is acid due to HCl, cobalt will cease to be attacked as soon as the fusion becomes alkaline. If some of the cobalt has been dissolved, and then Na_2CO_3 is added to produce alkalinity, a brown precipitate of cobalt oxide is formed. For some inexplicable reason the nickel cathode in one experiment, mentioned above, was not attacked. This experiment we have thus far not been able to duplicate, although many attempts were made to do so. More experiments were made using Na_2CO_3, H_3BO_3 and $Na_2B_4O_7$, respectively, as addition agents to the fusion. By thus using Na_2CO_3 to keep fusion neutral or slightly alkaline, several smooth deposits of tungsten metal were obtained, but they were always exceedingly thin. It appeared that when Na_2CO_3 was added to the fusion in sufficient quantity nearly to neutralize the HCl present a point could be reached where the nickel electrode was no longer attacked, and tungsten could be deposited in the thin sheet as desired. If Na_2CO_3 is added to alkalinity electrolysis produces no metallic deposit.

To determine when the fusion was faintly acid on account of

the presence of HCl was very difficult and required long practice. Cobalt oxide was used as the indicator. As long as the fusion was acid the indicator gave a blue coloration; when alkaline, the cobalt oxide separated out as a brown precipitate. The most favorable point for electrolysis could be found by the intensity of the color produced by the indicator. After the correct degree of acidity of the fusion has been reached, tungsten is deposited on the nickel cathode as a smooth, ductile deposit; but it was impossible to keep the fusion in the proper condition for more than fifteen minutes at a time. The current density in all of these cases was very low, about 0.015 amp. per sq. cm. Higher current densities always failed to produce the smooth deposit.

Some experiments using normal sodium tungsten, Na_2WO_4, were made in order to ascertain if a smooth deposit of tungsten could be obtained from a different type of fusion. It was found that if a small amount (1 gram) of WO_3 or H_2WO_4 was added to a fusion of 50 grams of Na_2WO_4, the fusion when electrolyzed with a nickel cathode and a carbon anode would give a smooth deposit of tungsten. However, this condition of the fusion lasts for only a few minutes, after which the metal begins to deposit as a black powder. From these facts it is evident that the formation of the smooth deposit of metallic tungsten is in no way dependent upon the NaCl or HCl in the other fusions, but is rather due to the presence of some acid tungstate, which is formed only in small amounts or decomposes soon after formation.

II. PREPARATION OF ALKALI TUNGSTEN BRONZES BY ELECTROLYSIS.

Fusions were also electrolyzed which contained more than 50 grams of H_2WO_4 to 100 grams of the NaCl-KCl mixture. When 100 grams of H_2WO_4 was added to 100 grams of the NaCl-KCl fusion, electrolysis failed to deposit any metal. Oxygen was evolved on the anodes as before, but at the cathode a deposit of beautiful blue needles was formed. This deposit proved to be an alkali tungsten bronze, $Na_2W_5O_{15}$ or $Na_2O.W_5O_{14}$. In other words, it is a compound of Na_2O with a lower oxide of tungsten. A red bronze, which has the formula $Na_4W_5O_{15}$ or $(Na_2O)_2.W_5O_{13}$ was also obtained. It was formed by electrolyzing a fusion prepared by

adding 60 grams of H_2WO_4 to 100 grams of the NaCl-KCl mixture. The red bronze deposited on the cathode.

If only 55 grams of H_2WO_4 were used in the fusion metallic tungsten was deposited by electrolysis. By increasing the H_2WO_4 content to 60 grams the red bronze was obtained, and by further increasing the H_2WO_4 and electrolyzing a violet bronze was formed. By varying the current density at the cathode these different bronzes could also be obtained. With increase of current density the bronze deposit changed from blue to violet and red, and finally with very high current densities to yellow.

III. PREPARATION OF TUNGSTEN BY METALLIC REPLACEMENT.

Experiments on the replacement of tungsten in fusions of H_2WO_4, NaCl and KCl were made. Zinc was added to a fusion made by using equal parts of H_2WO_4, NaCl and KCl. The zinc was rapidly attacked, forming ZnO and a black powder consisting of metallic tungsten. The mass was cooled, treated with water, and finally with dilute HCl. A deep blue color was formed when the acid was added. This was due to the fact that hydrogen was liberated by the action of the acid on the excess of zinc present, and this hydrogen reduced the excess of tungstates present to W_2O_5. Pure, finely divided tungsten was obtained by extracting the fusion with dilute NaOH, to remove the excess of tungstates, and then treating the residue with HCl to remove the zinc and zinc oxide.

When iron was used in place of zinc there was no reaction whatever. Aluminum, on the other hand, effected a more rapid reduction than did zinc. From these facts it would appear that in this fusion the position of tungsten in the electrochemical series lies between zinc and iron.

A large number of experiments were made to determine the conditions necessary for maximum yield when tungsten is replaced by zinc in the fusions described. The method of procedure was to add H_2WO_4 to a fusion of equal parts of NaCl and KCl, and then treat the fused mass with zinc dust. Much of the zinc burned in the air as it touched the surface of the fusion, so that a notable amount of its reducing power was lost. However, even when a larger excess of zinc dust was added to the fusion, the yield of metallic tungsten could not be increased beyond 30

per cent. The percentage yield of tungsten was not influenced by the amount of H_2WO_4 used, provided there was always an excess of zinc present, which was to have been expected. In fact there was always an excess of zinc and also of tungstates present after the reaction. The method of procedure was changed somewhat in the next experiment.

Equal parts of NaCl and KCl were mixed with the proper amount of zinc dust. This mixture was then heated to fusion. The zinc did not settle out, but remained in suspension. The proportions of zinc and H_2WO_4 used were according to the following equation:

$$H_2WO_4 + 3Zn = H_2O + 3ZnO + W.$$

The amount of H_2WO_4 taken was one-half of the weight of the NaCl-KCl mixture. The H_2WO_4 was added to the fusion of the NaCl-KCl and zinc. After half an hour of heating at a temperature of 800° C. the fusion was cooled and extracted with dilute NaOH and then with dilute HCl. The yield of metallic tungsten was 67 per cent of the theoretical in this case. Even when a large excess of zinc was used in a similar experiment the reduction was not complete. There was always an excess of zinc and of tungstates. There are two reasons for the low yield: (1) Zinc was occluded by tungsten and by ZnO, and (2) the HCl and Cl_2 evolved when the H_2WO_4 is added to the fusion attack the zinc.

The tungsten prepared by this method was in the form of a fine black powder, but it was pure.

IV. PREPARATION OF TUNGSTEN ALLOYS.

Three different methods may be used to prepare tungsten alloys employing NaCl-H_2WO_4 fusion as the source of tungsten.

(a) When the metal with which it is desired to alloy tungsten has a low melting point (below 800° C.) it may be used in the molten condition as a cathode, provided, of course, that it does not replace tungsten from the solution. This method is specially applicable in the formation of lead or tin tungsten alloys, and several such alloys were in fact produced in the course of this investigation.

(b) In the case of aluminum or zinc which replace tungsten in

the fusion, it is only necessary to add an excess of either of these metals to the fusion. Alloys of aluminum and tungsten and of zinc and tungsten were readily prepared by this method. While exact quantitative analyses of these alloys were not made, qualitative chemical analyses showed beyond any doubt that the alloys consisted of material amounts of zinc and tungsten and aluminum and tungsten, respectively.

(c) If an alloy of a metal such as nickel or cobalt is desired, a fusion of H_2WO_4 and NaCl is made and then NiO or $NiCl_2$ (in the case of nickel alloys) is added as either one dissolves readily in the fusion. The latter is then subjected to electrolysis, whereupon the nickel tungsten alloy is deposited on the cathode in beautiful shining needles. Both nickel tungsten and cobalt tungsten alloys were produced by this method, which no doubt can also be used to prepare a large number of other alloys.

Chemical Laboratory,
University of Wisconsin,
Madison, July, 1924.

DISCUSSION.

COLIN G. FINK[7]: I have been much interested in tungsten research for over 17 years, and I was very pleased to see Prof. Kahlenberg's paper. I was a little disappointed in not finding in the paper more metallographic studies. May I suggest that the authors in their further investigation be guided more by modern metallurgical methods than by mere control through chemical analysis. In that way I feel certain they will soon ascertain what the difference was between that little piece of ductile material they had and the other products which were so brittle. At the laboratory at Columbia we have been interested in obtaining tungsten from the aqueous baths. It is a curious fact that of the four metals of the group to which tungsten belongs, namely, chromium, molybdenum, tungsten and uranium, molybdenum and tungsten are comparatively readily reduced by common reducing agents, such as hydrogen and carbon monoxide, whereas chromium oxide is reduced with considerable difficulty. On the other hand,

[7] Head, Division Electrochemistry, Columbia University, New York City.

chromium oxide will readily reduce electrolytically in an aqueous bath, whereas tungsten oxide in an aqueous bath is reduced with difficulty. The conditions for tungstic acid in an aqueous bath have not been worked out as carefully and diligently as the conditions have been worked out for chromic acid. In view of the fact that the metals, chromium and tungsten, belong to the same group, I have full confidence that we will some day get pure tungsten from an aqueous bath without any great difficulty. One of my students, Mr. Sobel, who has been conducting the work on the aqueous electrolytes for the production of metallic tungsten, has been getting some nice deposits.

Louis Kahlenberg: As concerns chromium and tungsten, although they belong to the same group in the periodic system, they are quite different metals. We know the Secretary presented to us some interesting things on the deposition of metallic chromium from his laboratory, but we have made efforts to deposit metallic tungsten from aqueous solutions, and so far have failed. We hope you will be able to do that at Columbia.

B. D. Saklatwalla[8]: In reference to Dr. Fink's remarks on the reducibility of chromium oxide by hydrogen, I think there is a recent work published in the Zeitschrift für Metallkunde, where the reduction of chromium tri-oxide has been accomplished by hydrogen. This work proves that the difficulty lay in not having the hydrogen pure enough. If hydrogen is purified to a very high degree of purity, the reduction of chromium oxide does take place at ordinary pressure. The author of this article realizes the uncommercial aspect and the high cost of such procedure, nevertheless, it is of theoretical interest to us to know that such reduction does take place.

Colin G. Fink: If you take tungsten oxide and use absolutely pure hydrogen your reduced metal is nice and soft and ductile, but with the merest trace of oxygen in the hydrogen you get a brittle tungsten rod. The whole trick has been in the elimination of the last trace of oxygen.

Menahem Merlub-Sobel[9] (*Communicated*): In their criticism of the work of Messrs. Mann and Halvorsen,[10] Messrs.

[8] Vanadium Corp. of America, Bridgeville, Pa.
[9] Chemical Engineer, Columbia University, New York City.
[10] Trans. Am. Electrochem. Soc., **45**, 493 (1924).

Kahlenberg have suggested that the metallic plates obtained from an electrolysis using tungsten anodes and iron cathodes probably contain no small percentage of iron. This iron, admittedly present in the electrolyte, probably originated from the iron crucible rather than from the cathode, so that the use of copper as a cathode material, as in my own experiments in this field, would not be in itself sufficient to disprove this claim.

On the other hand, an experiment run in a porcelain crucible, with a copper cathode, thereby excluding any danger of iron contamination, gave plates which, as far as casual observation could discern, differed in no way from those run in iron crucibles.

The claim that a plate may contain considerable iron and still be unaffected by HCl, as indicated by the inertness of W_2Fe_3 to the action of HCl, is open to the serious objection that two metals deposited simultaneously do not necessarily form a chemical compound. The compound W_2Fe_3, in particular, is not likely, since it is not formed by direct combination, but, rather, indirectly, through the use of tungstic anhydride.[11]

The supposition expressed by the authors of the paper that the mere presence of iron in the electrolyte is sufficient to insure its deposition in the plate because "it is well known that iron is more readily deposited than tungsten" seems quite erroneous to me, both in fact and in hypothesis. Tungsten, according to Fischer,[12] lies in the electromotive series between Sb and Hg, both of which are considerably below hydrogen. According to his figures, Sb is +0.466, W is +0.609 and Hg is +0.750, with respect to zero hydrogen. Iron, on the other hand, is considerably higher than hydrogen, the elements being in the order Fe, Co, Ni, Sn, Pb and H, according to Smith's Inorganic Chemistry. We can therefore expect tungsten to be deposited out alone even in the presence of iron in the electrolyte, just as copper is deposited out under the same circumstances. The mere fact that tungsten, *in aqueous solution,* does not plate out more readily than iron is no indication whatsoever of the action in fused baths, since in aqueous solution hydrolysis is the sole difficulty, such hydrolysis yielding pseudo-metallic WO and WO_2 ions instead of W. No such phenomenon being possible in fused electrolytes, normal electromotive-series

[11] Mennicke, Die Metallurgie des Wolframs.

[12] See Koerner, Trans. Am. Electrochem. Soc., 31, 232 (1917).

behavior may be expected, and with tungsten so much below iron, no deposition of iron need be assumed in any such tungsten-plating bath.

L. and H. KAHLENBERG (*Communicated*): In stating that an alloy high in iron, such as W_2Fe_3, is not attacked by hydrochloric acid, we did not mean that an alloy of that composition was necessarily formed. Alloys may form according to the law of definite proportions, and consequently be perfectly definite compounds; but they may also form according to variable proportions, in which case they are so-called solid solutions. Alloys of iron and tungsten high in tungsten are not attacked by hydrochloric acid, and hence the fact that the deposit is not attacked by hydrochloric acid is no proof that it is pure tungsten.

The relative positions of the metals in the electromotive series as given by Mr. Sobel refer to aqueous solutions. The same is true of the tables given in Alexander Smith's Chemistry, and therefore these series do not apply at all to fused electrolytes. As a matter of fact, we have found, experimentally, that in a fusion of equal parts of sodium and potassium chlorides, iron is only slightly higher than tungsten, being about 0.02 volt, the current flowing from the iron through the electrolyte to the tungsten. Since this difference is so very small, the iron and tungsten would undoubtedly deposit simultaneously during electrolysis.

In the type of fusion which we used, namely tungstic acid dissolved in fused alkali chlorides heated till all hydrochloric acid is expelled, the polarity of iron and tungsten electrodes is reversed, that is to say the current flows from the tungsten through the electrolyte to the iron, the e. m. f. of the cell being 0.13 volt. Under these circumstances iron certainly would be more readily deposited than tungsten, which agrees also with the fact that iron will not replace tungsten in such fusions.

COLIN G. FINK (*Communicated*): The article in Zeitschrift für Metallkunde[13] to which Dr. Saklatwalla refers describes an elaborate method for the purification of hydrogen, and the reduction of chromic oxide with this pure hydrogen. Back in 1907 and 1908, when I was engaged in the research on ductile tungsten, I found that the least trace of moisture or oxygen in hydrogen can

[13] "Die Darstellung reinen Chroms durch unmittelbare Reduktion des Oxydes mit Wasserstoff," by W. Rohn, Z. f. Metallkunde, **16**, 275, July, 1924.

be removed or "rendered harmless" by a method much more practical than that of Rohn, and requiring only simple apparatus. I found that the introduction into the impure hydrogen of a definite quantity of a hydro-carbon gas counteracted the deleterious effect of traces of oxygen or moisture. By this method I was able to produce soft, malleable, ductile tungsten metal by heat treatment alone, a method quite distinct from the earlier method I had worked out, the ductilization by hot mechanical treatment. In view of what Rohn has found, it seems most probable to me that the application of my method to the reduction of chromic oxide ought to meet with success. At all events we are now engaged in trying this out.

A paper presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 4, 1924, President Parmelee in the Chair.

HALOGENATED HYDROCARBONS AS DIELECTRICS.

Effect on Flash and Fire Point of Transformer Oils.[1]

By H. C. P. Weber and R. H. Wynne[2]

Abstract.

In order to determine what regularities, if any, existed in the effect of halogenated hydrocarbons upon combustible oils, a study was made of the change in flash and fire points produced by varying percentages of a series of compounds. The oils were two transformer oils designated, respectively, "Lectroseal" and "Hi Flash" oils.

The list of halogenated compounds used is given in Table I. The list comprises a number of aliphatic and aromatic hydrocarbons, mostly chlorides, which are well known.[3] Halowax oil and halowax are trade names for compounds used to some extent as insulating media. They are, as the names indicate, oily and waxy substances, consisting essentially of chlorinated naphthalines.

The "snuffer," as the halogenated material may be called for short, was added to the extent of 5, 10, 20 and 40 per cent of the oil by volume. Table I gives the results for "Lectroseal" oil and Table II similar values for "Hi Flash" oil. Both of these oils are petroleum fractions, in which paraffine hydrocarbons predominate, with an average composition of $C_{14}H_x$ to $C_{16}H_x$.

The flash and fire points were determined by the open cup method.

[1] Manuscript received July 14, 1924.

[2] Westinghouse Elec. & Mfg. Co., East Pittsburgh, Pa.

[3] We are indebted to the Commercial Solvents Corporation, the Dow Chemical Company and the Hooker Electrochemical Company for samples, which they supplied for examination.

Tables I and II show that there is some proportionality between the percentage of "snuffer" added and the raising of the flash point. In the case of the lower boiling addition agents, the evaporation loss during the flash point test is appreciable. This causes some lowering of the apparent effectiveness.

TABLE I.

Effect of Halogenated Compounds on Flash and Fire Points of Oil.

Lectroseal Oil: Flash Point 140° C., Fire Point 166° C.

Addition, by volume	5 Per Cent		10 Per Cent		20 Per Cent		40 Per Cent	
	Flash	Fire	Flash	Fire	Flash	Fire	Flash	Fire
	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.
Dichlormethane	143	170	144	170	144	170	145	170
Chloroform	144	169	148	170	161	174	171	178
Carbon tetrachloride	148	166	167	173	183	187	185	188
Tetrachlorethane ..	139	174	152	183	179	193	194	205
Hexachlorethane ...	164	175	175	202	207	219	235	240
Tetrachlordibromethane	...	...	196	203	...	...	...	...
Dichlorethylene	...	...	43	160	...	...	...	...
Tetrachlorethylene .	139	170	163	179	174	186	195	203
Ethylene bromide ..	162	183	200	212	210	216	...	...
Monochlorbenzene .	95	147	70	125	...	...	...	...
Ortho dichlorbenzene	...	...	110	157	...	...	...	...
Para dichlorbenzene	...	...	136	155	...	...	...	...
Monobrombenzene..	...	...	93	190	...	...	...	...
Halowax oil	141	165	140	166	134	165	130	165
Halowax 1004	139	170	147	170	181	200	221	253
Chlorethyl acetate ..	...	...	75	118	...	...	...	...
Ethyl chloracetate..	...	...	72	106	...	...	...	...

Tetrachlordibromethane gave irritating vapors and considerable carbonization of the oil, and is therefore not of any practical interest.

In Table III the composition and percentage of halogen of the compounds used is shown; further the flash or firing point of the snuffer itself, and the effect of a 10 per cent addition (by volume) upon the flash and fire point of two oils. (Thus + 4 indicates that the flash point has been raised 4° C.). Under the halogenated hydrocarbon itself "extinguishes flame at ° C." indicates that when the snuffer is heated to the point stated the 0.5 in. flame of

the small gas torch used to make the flash test is extinguished when brought over the surface of the liquid.

Inspection of Table III brings out the following facts: Halogenated compounds, which flash at temperatures below the normal flashing temperature of the oil, lower the flash point of this

TABLE II.

Effect of Halogenated Compounds on Flash and Fire Points of Oil.

Hi Flash Oil: Flash Point 185° C. Fire Point 215° C.

Addition, by volume	5 Per Cent		10 Per Cent		20 Per Cent		40 Per Cent	
	Flash	Fire	Flash	Fire	Flash	Fire	Flash	Fire
	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.
Dichlormethane	184	217	183	220	184	221	183	222
Chloroform	185	217	185	218	185	220	185	222
Carbon terachloride	188	218	190	221	198	223	205	223
Tetrachlorethane ...	180	221	185	222	218	228	218	229
Hexachlorethane ...	189	222	198	225	233	241	250	257
Tetrachlordibromethane	...	...	200	220	...	...	...	...
Dichlorethylene	...	...	42	215	...	...	...	...
Tetrachlorethylene..	180	217	190	220	196	220	201	222
Ethylene bromide...	200	224	206	226	221	234	...	...
Monochlorbenzene..	...	...	80	215	...	...	...	...
Ortho dichlorbenzene	...	...	118	211	...	...	...	...
Para dichlorbenzene	...	...	146	210	...	...	...	...
Monobrombenzene .	...	...	95	230	...	...	...	...
Halowax oil	...	...	163	215	...	...	...	...
Halowax 1004	190	226	190	236	195	237	228	241
Chlorethyl acetate ..	...	...	81	215	...	...	...	...
Ethyl chloracetate .	...	...	75	140	...	...	...	...

oil. This is as was to be expected. Conversely those which flash at a temperature higher than that of oil, or extinguish flame at or near their boiling point, raise the flash point of the oil.

Changes in the fire point are as a rule parallel to the changes in the flash point, but not so marked. An apparent exception to this is monobrombenzene, which lowers the flash point, but raises the fire point of both oils.

Of the compounds in the list, those which extinguish flame at their boiling point, all contain over 80 per cent halogen.

TABLE III.—*Composition of Compounds, and Change Effected on Flash and Fire Points of Oils.*

Addition	Formula	Per Cent Halogen	Density	Boiling Point	Extinguishes Flame at ° C.		Effect of Addition of 10 Per Cent by Volume			
							on Lectroseal Oil		on Hi Flash Oil	
							Flash	Fire	Flash	Fire
							° C.	° C.	° C.	° C.
Dichlormethane	CH_2Cl_2	83.5	1.37	42	41		+4	+4	—2	+5
Chloroform	$CHCl_3$	89.1	1.47	62	62		+8	+4	0	+3
Carbon tetrachloride	CCl_4	92.2	1.60	77	77		+27	+7	+5	+6
Tetrachlorethane	$C_2H_2Cl_4$	84.5	1.58	143	130-143		+12	+17	0	+7
Hexachlorethane	C_2Cl_6	89.9	2.00	185*	....		+35	+36	+13	+10
Tetrachlordibromethane	$C_2Cl_4Br_2$	92.6	2.70	185†	....		+56	+37	+15	+5
Tetrachlorethylene	C_2Cl_4	85.5	1.63	121	95-123		+23	+13	+5	+5
Ethylenebromide	$C_2H_4Br_2$	85.1	2.20	132	....		+60	+46	+21	+11
					Flash	Fire				
Dichlorethylene	$C_2H_2Cl_2$	73.2	1.25	37	17	60	—97	—67	—143	0
Monochlorbenzene	C_6H_5Cl	31.6	1.10	132	39	74	—70	—41	—105	0
Ortho dichlorbenzene	$C_6H_4Cl_2$	48.3	1.32	179	77	173	—30	—9	—67	—4
Para dichlorbenzene	$C_6H_4Cl_2$	48.3	1.27	174	78	171	—4	—11	—39	—5
Monobrombenzene	C_6H_5Br	51.0	1.50	156	65	+156	—47	+24	—90	+15
Halowax Oil	$C_{10}H_7Cl$	22.0	1.20	...	128	225	0	—6	—22	0
Halowax, 1004	$C_{10}H_2Cl_6$	64.0	1.70	...	263	+360	+7	+4	+5	+21
Chlorethyl acetate	$CH_3COOC_2H_4Cl$	29.0	....	121	67	82	—65	—48	—104	0
Ethyl chloracetate	$CH_2ClOOC_2H_5$	29.0	1.16	144	54	67	—68	—60	—110	—75

* Sublimes. † Sublimes and decomposes.

The effect of "snuffers" containing over 80 per cent halogen was more marked on "lectroseal" oil than on "hi flash." This is to be expected since "lectroseal" is a somewhat lighter oil.

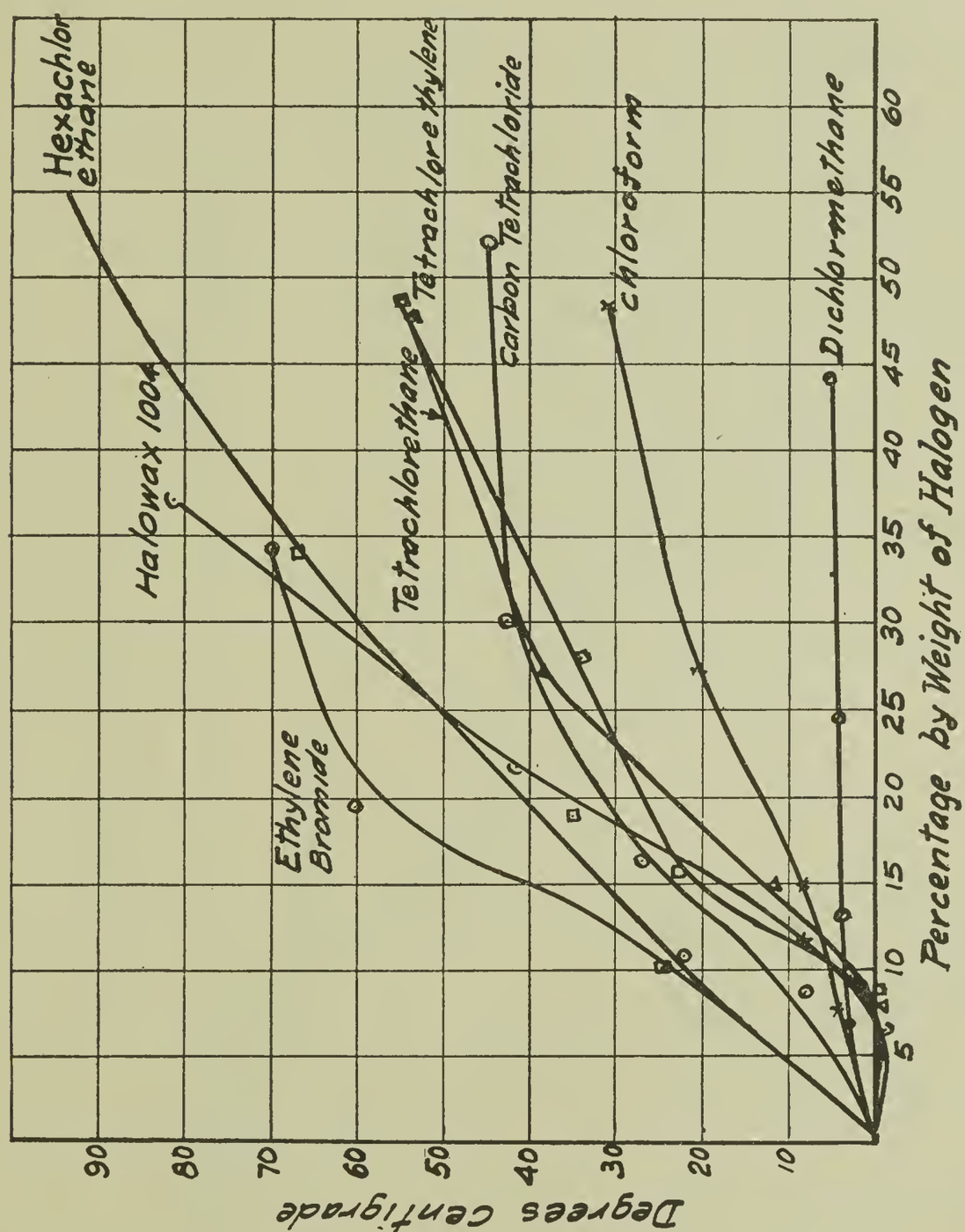


Fig. 1. Increase in Flash Point. Lectroseal Oil.

The most marked increases in flash and fire points are obtained with 80 per cent halogen compounds, which have the higher boiling points, namely, tetrachlorethane, hexachlorethane, tetrachlordibromethane, tetrachlorethylene and ethylene bromide. However, CCl_4 gives as large an increase as the higher boiling tetrachlorethane, which contains about 7 per cent less chlorine.

The low boiling high halogen content "snuffers" are largely driven out of solution before the flash and fire points are reached.

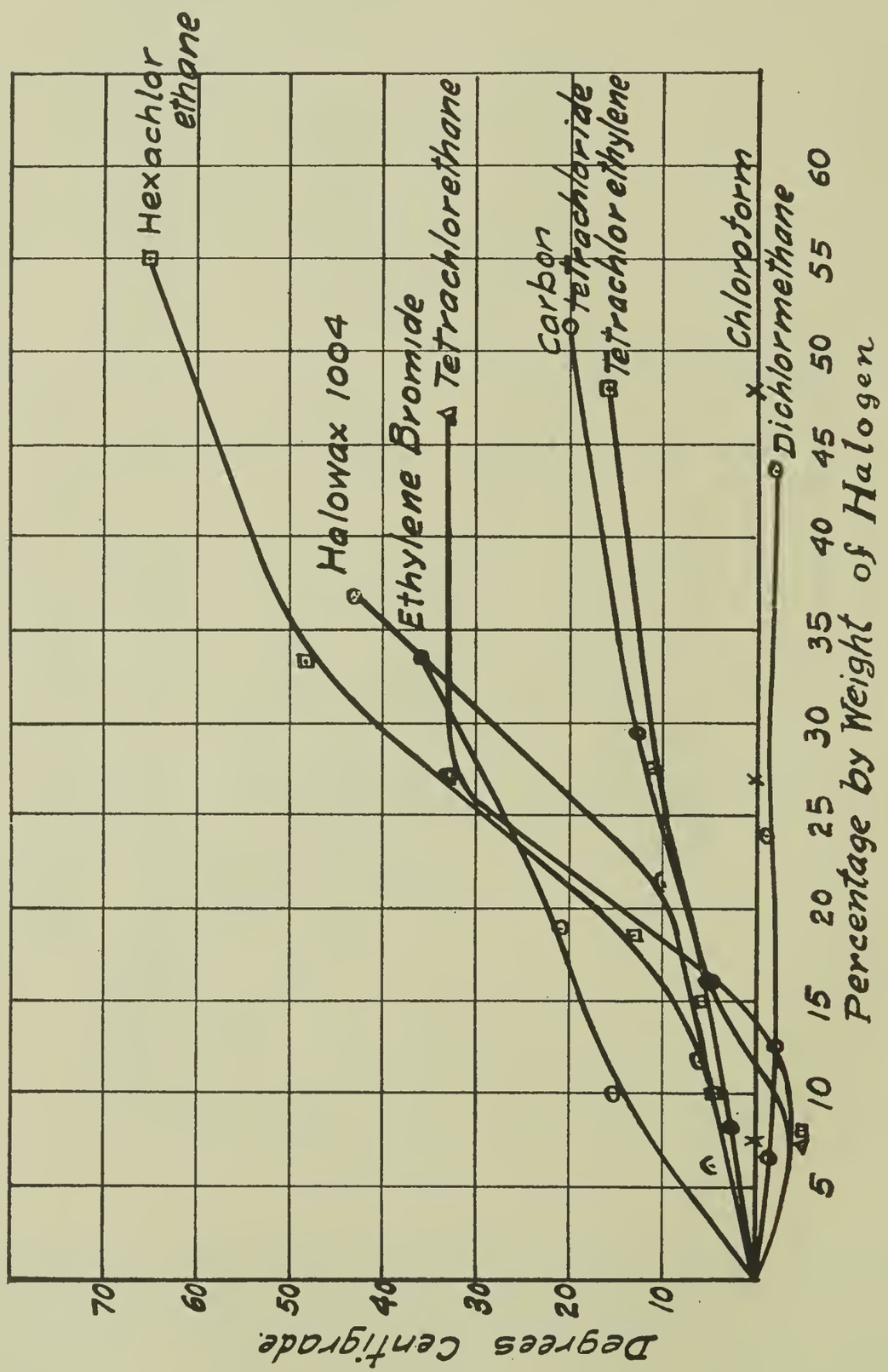


FIG. 2. Increase in Flash Point. Hi Flash Oil.

Under conditions where evaporation is prevented the most volatile snuffers would of course be the most effective.

In the two sets of curves (Fig. 1 and 2) raising of the flash point is plotted against the percentage of halogen by weight. These curves show that the raising of the flash point is not directly proportional to the amount of halogen added to the oil. In the case of "lectro-seal" the greatest proportional effect is found to range from 10 to 30 per cent, with possibly a maximum at 20 per cent. In the case of the higher boiling "hi flash," the greatest effect is found to be near 30 per cent. For reference, a 10 per cent volume addition may in most cases be taken as equal to 15 per cent by weight.

Of the compounds examined, those containing bromine raise the flash point more than compounds containing an equal weight of chlorine.

The choice of a "snuffer" for reducing the flammability of oils would depend largely on the application. Where evaporation can take place readily, the snuffer should have as high a boiling point as possible. For closed containers the lower boiling compounds are desirable. The comparison of snuffers for such use should be carried out with closed cup tester.

Further comparisons as to corrosive effects and dielectric behavior of mixtures of snuffers and oils are planned.

DISCUSSION.

E. A. Snyder[4] (*Communicated*): The above paper points out that certain halogenated hydrocarbons, when mixed with transformer oil, act as "snuffers." About a year and a half ago we conducted a large number of tests at the Pittsfield Works of the General Electric Company, to determine the possibility of using halogenated hydrocarbons, either alone or mixed with oils, in the operation of transformers.

The results of our tests showed conclusively that the material was not suitable, because, first of all, these hydrocarbons were all highly corrosive in their action and had a very deleterious effect on the insulating varnish on the coils and greatly corroded the transformer tanks and covers.

Secondly, the hydrocarbons when used in connection with transformer oils caused the oils to sludge excessively. One transformer,

[4] Pittsfield Works Laboratory of General Electric Co., Pittsfield, Mass.

which was operated on a mixture of oil and halogenated hydrocarbons, when opened after a comparatively short test run, was found to be full of a large amount of slimy sludged deposit, and the covers and sides of the tank and the insulation had been very much attacked by the corrosive action of the hydrocarbons.

While it is true that many of these halogenated hydrocarbons do tend to lower the flash point of transformer oils, it is also true that it is practically impossible to keep them in the oils. They are usually more volatile than the oil, and the ratio of the halogenated hydrocarbons to oil is constantly changing.

A paper presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 4, 1924, President Parmelee in the Chair.

THE RELATION BETWEEN CURRENT, VOLTAGE, AND THE LENGTH OF CARBON ARCS.

III—Alternating Currents.[1]

By A. E. R. Westman[2] and R. B. Walker.[2]

Abstract.

Papers I[3] and II[4] gave the results of an investigation of the relation between current, voltage and arc length for carbon arcs carrying direct currents of from 100 to 700 amp. This paper reports a similar investigation in which *alternating* currents of like magnitude were used. The current and voltage wave forms are also given and their significance discussed.

INSTRUMENTS AND APPARATUS.

The electric furnace laboratories of the University have a 200 k. v. a., single phase, 25-cycle, 125-volt installation operated from the Ontario hydro-electric power system;[5] this was used in all but a few runs in which an 18 k. v. a., 120-volt, 60-cycle alternator was used. Both petroleum coke and anthracite coal base electrodes, manufactured by the National Carbon Co., were used. The series rheostat, graphite voltmeter contacts, cathetometer, cathode guide, observation screen, anode clamp, and cooling apparatus were the same as described in the preceding papers, and the method of procedure was essentially that already described in detail. The use of alternating current, however, necessitated the following changes:

The Furnace. The "magnetic shield" (paper I, p. 176), which with alternating currents would overheat and introduce reactance

[1] Manuscript received May 3, 1924.

[2] University of Toronto, Toronto, Ont., Canada. The three papers on arcs constitute a thesis submitted by A. E. R. Westman for the degree of Doctor of Philosophy.

[3] Paper I, Trans. Am. Electrochem. Soc., 43, 171 (1923).

[4] Paper II, Trans. Am. Electrochem. Soc., 44, 137 (1923).

[5] Can. Chem. and Met., 5, 224 (1921).

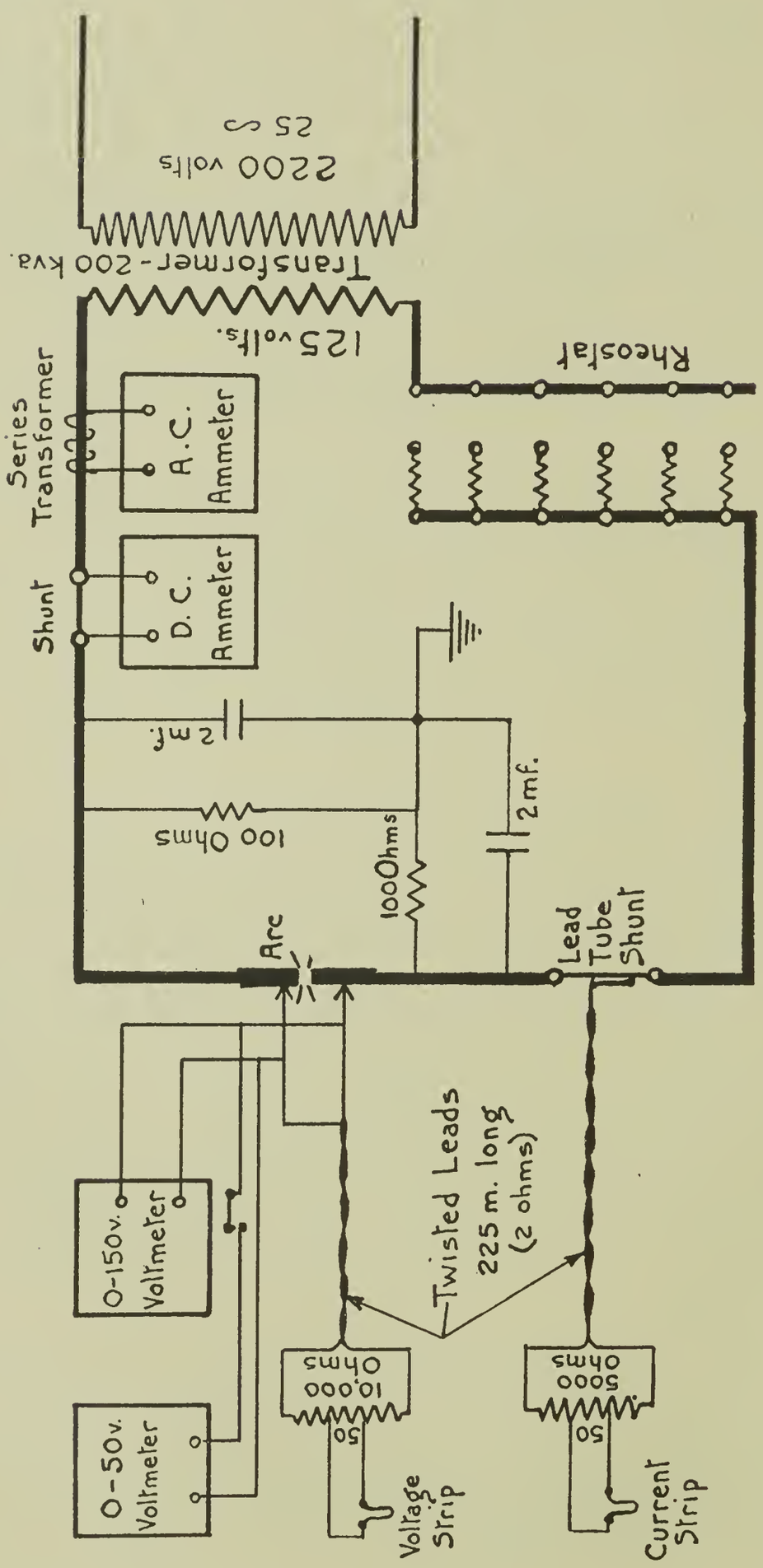


Fig. 1. General Wiring Diagram.

and other magnetic complications, was removed and a similar structure of clay firebrick inserted to keep the air currents as before. Between this structure and the shell of the furnace we installed two electromagnets with cores 4 cm. in diameter, and with windings of about 60 turns of asbestos insulated copper wire, which could be operated by direct current (10 amp.) to produce a stationary magnetic field at right angles to the arc. At the same time arrangements were made for a mica window which could be used in the shorter runs for observing the arc from the side.

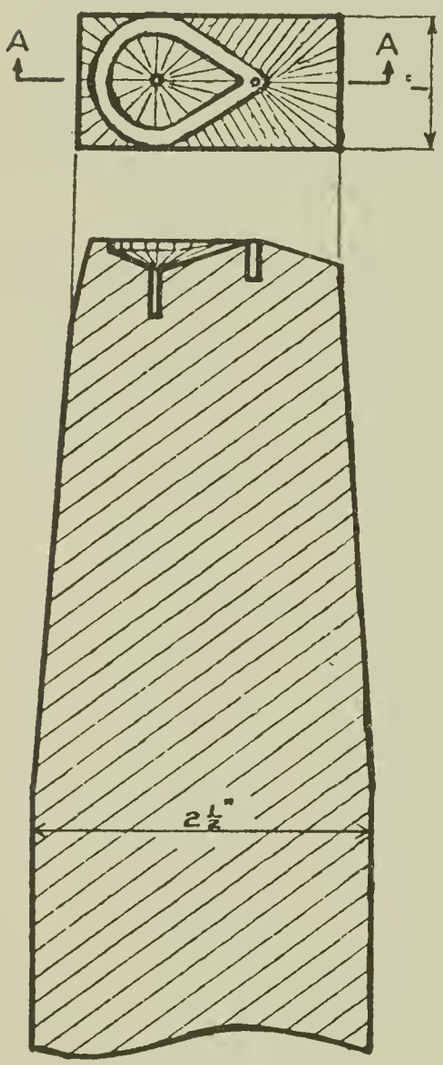
Voltmeters. The previous arrangement of voltmeters (I, p. 171) was abandoned, and two model 155 Weston a. c. voltmeters (0-50 v. and 0-150 v.) were used (Fig. 1). The 0-50 v. meter was sufficiently sensitive for this work, and could be connected across the graphite voltmeter contacts by means of a switch when the 0-150 v. meter showed that the arc voltage was less than 50 v.

Ammeters. A Packard 1,000/5 current transformer, and a Westinghouse type S. M. switchboard ammeter, calibrated by means of a model 461 Weston portable current transformer and a model 155 Weston portable ammeter, were used in measuring currents above 200 amp.; for currents less than this the portable instruments themselves were used. To detect rectification, a d. c. millivoltmeter was connected across a 750 amp. shunt in series with the arc; it did not show any deflection in any of the runs.

Oscillographs. A Siemens-Blondel standard two-element oscillograph was used in most of the work, but to obtain a negative with sufficient contrast for reproduction we used a General Electric oscillograph, which had been fitted with a powerful lamp.

In making the oscillograms, one element of the oscillograph was connected through suitable non-inductive, no-capacity resistances to the graphite voltmeter contacts, and the other (through similar resistances) across a 0.003 ohm shunt made of water-cooled lead tubing (6.4 mm. outside, 4.8 mm. inside diameter), which was connected in series with the arc, and could be short-circuited by a heavy knife switch when not in use. The average temperature rise of this shunt when carrying 700 amp. was only 3° C. per min., so that no appreciable distortion of the oscillogram could result from changes in its temperature during an alternation. As both

the oscillographs were situated at some distance from the furnace (76 and 152 meters, respectively), there was some danger that the long leads might act as an oscillatory circuit, and develop a high voltage across the oscillograph element. To guard against this, twisted leads were used, and two small condensers (2 microfarads), connected in series and provided with a grounded neutral point, were connected across the arc. As there was also danger of a high voltage developing between the element and the ground, two wire resistances (100 ohms) were similarly connected (see Fig. 1). A temporary telephone circuit was set up between the furnace room and the oscillograph so that the meter readings corresponding to the oscillograms could be secured.



Section A-A

Fig. 2.

Electrode showing crater and tip.

EXPERIMENTAL CONDITIONS.

Starting the Arc. As in the previous work (paper I, p. 176), the arc was started in all cases by means of powdered carbon.

Electrode Dimensions—Split Arcs. In all the runs both upper and lower electrodes were of the same shape. To determine the best electrode dimensions preliminary runs were made, using electrodes with ends tuned flat in a lathe. The arc so formed was very unsteady, making a deafening noise and shrieking continually. From observations of the arc and the shape of the electrodes after a run, we concluded that under ordinary conditions the alternating current arc splits into two parts, the current path changing with each alternation and causing one or more corresponding anode craters and cathode tips to form on each electrode.[6] Accordingly, we tried the effect of forming a crater and

[6] A similar observation was made by O. P. Watts (Bull. 7, Wisconsin Univ., Fig. 3, p. 308 (1903). We have also been shown electrodes of this form by Mr. Kelleher in the Fitzgerald Laboratories, Inc., Niagara Falls, N. Y.

tip on each electrode and eventually developed the dimensions shown in Fig. 2. With these dimensions, by keeping the arc length small (2-10 mm.), a fairly steady arc was secured for periods of about 20 minutes. In the runs with low currents (150 amp.) these dimensions were halved.

Sometimes, however, the arc split in such a manner that our preformed craters acted as cathodes. This gave rise to a very unsteady arc, and was prevented by means of the electromagnets already described which were used to create a stationary magnetic field across the arc for the first few minutes of the run. The carbons were adjusted so that the line between the preformed cathode and anode on each electrode was at right angles to the line joining the two magnets.

Although with this procedure we succeeded in eliminating all shrieking, there still remained a low buzzing somewhat similar to that of a "humming arc," which we could not get rid of and which we finally decided was characteristic of this type of arc, *i. e.*, the "split arc." With arc lengths greater than about 10 mm. the arc always lost its split appearance and blew out to the side.

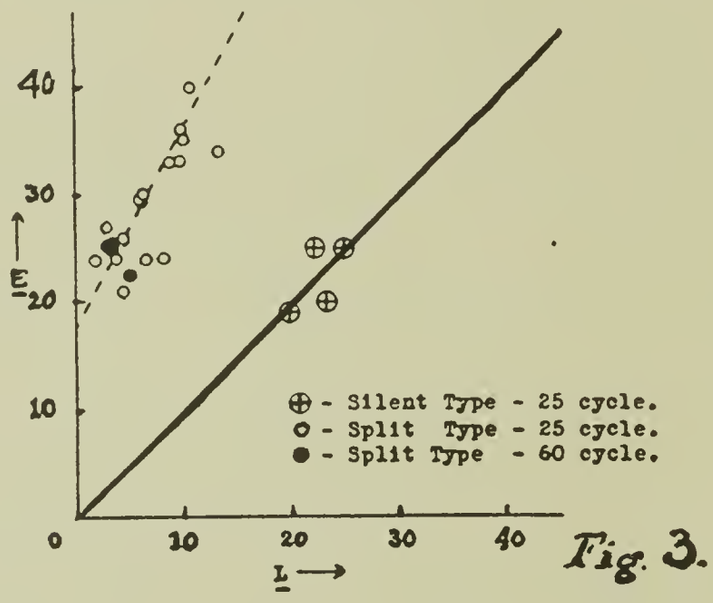
Electrode Dimensions—Silent Arcs. An attempt was made to develop electrode dimensions that would keep the arc from splitting. This led to the use of electrodes, both of which were shaped like the anode shown in paper II, p. 141, Fig. 3, the crater being 2.5 cm. in diameter for 700 amp. arc. With these dimensions we were able to secure a "silent arc." Observation of the arc through mica windows showed that it went from the bottom of the crater in one electrode to the bottom of the crater in the other, and this conclusion was confirmed by the fact that the electrodes, after a run, approximated the shape shown in dotted lines in the diagram referred to above. However, after the "silent arc" had been running for eight or nine minutes, arcing commenced between the rims of the craters, and almost immediately the arc left the craters and shrieked, and the voltage rose about 20 volts.

As both these types of arc required relatively small craters and tips, the labor involved in shaping the electrodes for a run was considerably lessened by using electrodes 2.5 in. (6.4 cm.) in diameter instead of 4 in. (10.2 cm.) in diameter as heretofore. Although this resulted in high current densities (150 amp. per

sq. in. or 23.3 amp. per sq. cm.), the electrodes did not crack if the current at the first of the run was built up at a rate not exceeding 10 amp. per sec.

MEASUREMENTS.

Determination of L-Split Arcs. With split arcs the electrodes burned away rapidly (the voltage with 700 amp, rising at a rate of about 3 v. per min. as compared with 0.33 v. per min. with steady d. c. arcs), and it was generally necessary to lower the upper electrode every five or ten minutes to keep the arc steady. When the voltmeter readings had been steady (no flickering)



Voltage *vs.* Arc Length.

for about fifteen or twenty minutes, and the arc emitted only a muffled buzz, the 0-50 voltmeter was read, the arc circuit broken, and a plaster model made as described in paper II, p. 143. With longer runs than this, laminated coatings of graphite, 3-4 mm. thick, formed on the electrodes, especially when anthracite coal base electrodes were used, which we considered detracted from the significance of our results. After most runs each electrode showed a distinct cathode tip and anode crater; the cathode tips, which with 700 amp. were about 5 mm. in diameter, showed a very bright metallic luster when rubbed with the finger, and were surrounded by depressions in the electrode, which were not coated with graphite. The corresponding anode craters, which were about 2 cm. in diameter, although they had a smooth graphite sur-

face, would not polish so brightly and were surrounded with a thin wall of graphite about 1 cm. high which had been built up by the arc. It was evident that with each alternation the arc stream went from a cathode tip to the corresponding anode crater and was reflected back, building up a wall around the crater and burning out the depressions around the cathode tip; in order to conform with our previous definition (I, p. 180; II, p. 144), we defined L for a split arc to be the distance in mm. from a cathode tip to the bottom of the corresponding anode crater. Thus each plaster model measurement gave two values of L; but when the arc was steady enough for measurement these proved to be equal within the limits of experimental error.

Working in this way L could be determined within a millimeter or two; but as split arcs could not be maintained at a length over 10 mm., and as they were never so steady as those obtainable with direct current, the accuracy and reproducibility of the determinations of L are not nearly so great as those reported in paper II. For this reason no attempt was made to correct for the small errors introduced by the contraction of the electrodes on cooling (about 0.5 mm. in L), and by the resistance of the portions of the electrodes between the graphite contacts and the arc (about 1 volt in E), more particularly as these two errors tended to offset each other. The results of twenty measurements are given in Table I and Fig. 3; in the latter the full line gives the relation between voltage and arc length found for d. c. arcs (viz. 0.99 v. per mm.), while the dotted line has been drawn through the points found experimentally for split arcs.

The relation connecting the arc length (L) and the voltage (E) as recorded on an a. c. voltmeter is given by

$$E = 18 + 0.9L \qquad (1)$$

Study of the oscillograms, such as Fig. 4, shows that E is practically identical with E_m the (almost) constant maximum voltage over the arc during the middle of each alternation, when, according to the interpretation given later, the current is being carried by an actual "arc" as distinguished from "gaseous conduction." Thus for split arcs;

$$E_m = 18 + 0.9L \qquad (2)$$

Determination of L—Silent Arcs. With silent arcs the conditions approached those under which the d. c. measurements were made, the voltage readings being very steady, and rising at a rate of about 0.75 volt per minute. As already noted, however, we did not find it possible to maintain an arc of this type for longer

TABLE I.

Characteristics for Split and Silent Arcs.

Run No.	Electrode		Arc Type	Frequency Cycles	*I* amp.	*E* v.	*L* mm.
	Base	Diam. cm.					
6	An. Coal	10.2	Split	25	750	30.0	5.7
8	" "	"	"	"	740	21.0	4.8
9	Pet. Coke	"	"	"	740	24.0	2.0
10	" "	6.4	"	"	680	40.0	10.8
12	" "	"	"	"	690	35.0	10.3
13	" "	"	"	"	750	33.0	9.0
14	" "	"	"	"	690	36.0	10.0
15	" "	"	"	"	700	34.0	13.5
16	" "	"	"	"	660	33.0	10.0
17	" "	"	"	"	680	29.0	6.5
24	" "	"	"	"	260	24.0	6.7
25	" "	"	"	"	100	26.0	4.6
26	" "	"	"	"	150	24.0	8.2
27	" "	"	"	"	580	29.5	6.3
32	" "	"	"	"	135	27.0	3.0
34	" "	"	"	"	680	24.0	4.0
28	" "	"	"	60	147	22.5	5.2
29	" "	"	"	"	135	25.5	3.9
30	" "	"	"	"	136	25.5	3.4
31	" "	"	"	"	131	25.0	3.7
18	" "	"	Silent	25	700	25.0	22.4
19	" "	"	"	"	700	20.0	19.0
22	" "	"	"	"	670	20.0	23.5
23	" "	"	"	"	630	26.0	25.0

than 8 or 9 minutes, of which the first two were needed to burn out the carbon powder used in starting the arc. In every case we let the arc burn until it suddenly left the crater, whereupon the circuit was broken and *L* determined as before. During the run the 0-50 voltmeter was read every minute and the last reading before the jump was recorded as the value of *E*. The results of four such determinations are given in Table I and Fig. 2. The

relation between L and E for arcs of this type is evidently much the same as for d. c. arcs; so that for silent arcs

$$E = 0.99L \tag{3}$$

and as before

$$E_m = 0.99L \tag{4}$$

Measurement of dE/dI for Constant L—Split Arcs. Several runs were made with split arcs during which the current was suddenly reduced by increasing the external resistance in series with the arc; in every case the decrease in current was accompanied by a temporary fall in voltage over the arc, but after burning for a few seconds or minutes at the new amperage, the original voltage was regained. When for instance the current was suddenly reduced from 750 amp. to 650 amp. the voltage dropped about 2 v., but returned to its former value in about 3 sec. With greater decrease in the current the drop was greater. Thus when the current was changed suddenly from 750 amp. to 200 amp. the voltage dropped about 6 v. and required about 10 sec. to regain its former value; and when the current was suddenly reduced from 700 amp. to 150 amp. the voltage fell from 28 v. to 10 v., and required nearly two min. to rise again to 28 v., at which it remained.

In the latter case, when the voltage dropped, the buzzing (characteristic of split arcs) stopped, the arc between the electrodes disappeared, and if it had not been for the meter readings we would have thought that the circuit had been broken. The arc, however, reappeared and the arc started again when the voltage had risen to about 15 v. During the silent interval it seems reasonable to ascribe the flow of current to "gaseous conduction" of some kind, quite different from that obtaining during the passage of an arc.

As the voltmeter gave merely the root mean square of the voltage, oscillograms were made: Fig. 4 (both voltage and current waves) while the current as read on the meter was 680 amp., Fig. 5 (voltage wave only, redrawn) immediately after reducing it to 150 amp. (voltmeter reading 10 v.), and Fig. 6 (voltage wave only, redrawn) a little later when the voltmeter reading had risen to about 15 v. and the noise was commencing again.

The oscillogram shown in Fig. 4 differs from the oscillograms made by previous experimenters using small currents, in that the voltage wave "jogs," that is, goes through a point of zero inflection, where it crosses the zero line and the instantaneous current reaches an appreciable magnitude (about 300 amp.) before the horizontal part of the voltage wave commences.

The voltage wave in Fig. 5, taken while the arc was extinguished, is characterized by the absence of a flat top, and by a

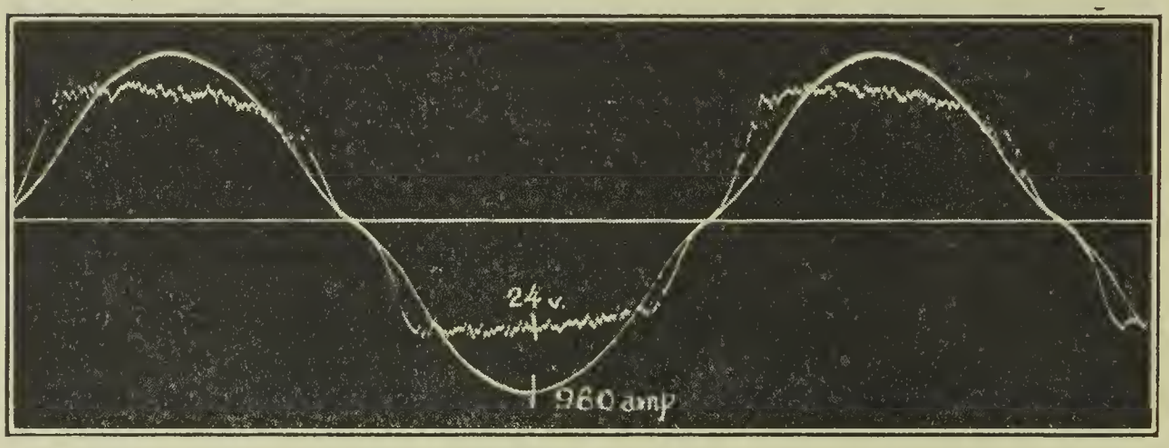


Fig. 4. Voltage and Current Waves. Split Arc.

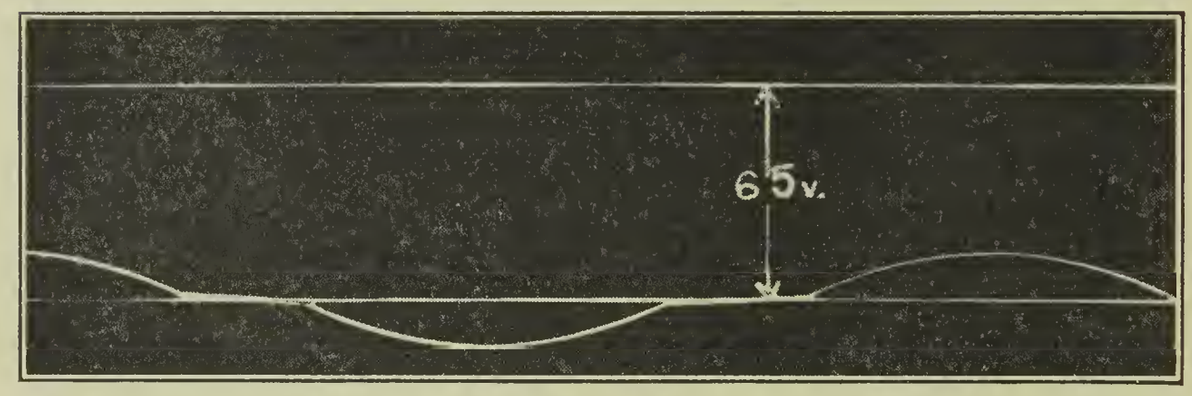


Fig. 5. Voltage Wave only; at 150 amperes; arc extinguished. "Gaseous Conduction."

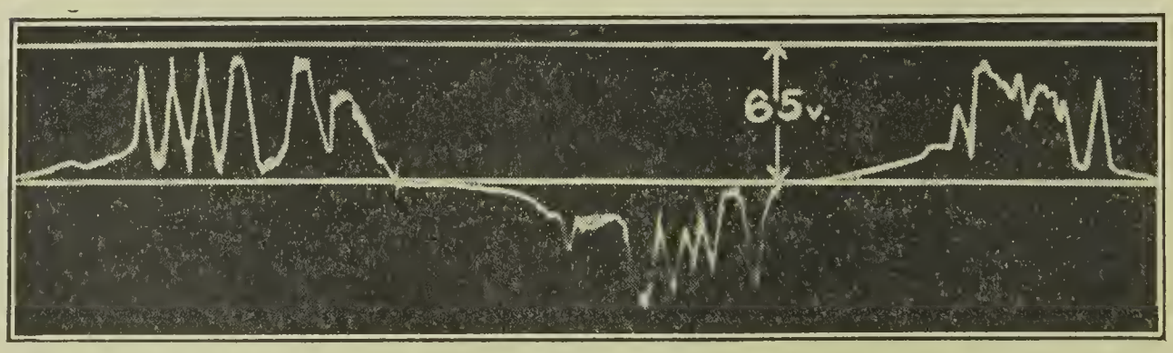


Fig. 6. Voltage Wave only. Intermediate stage. Split Arc.

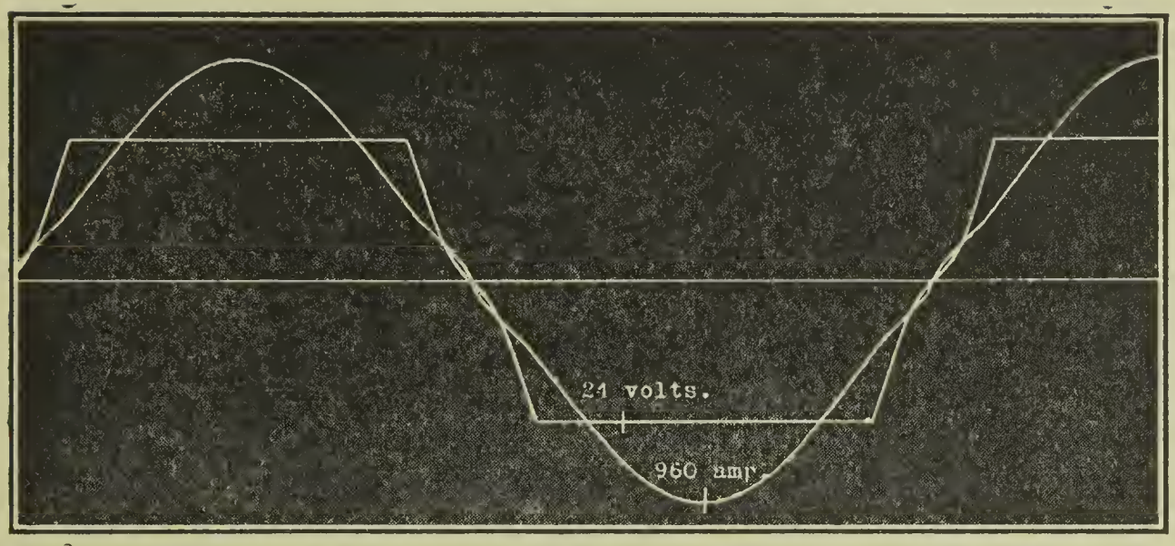


FIG. 7. Voltage and Current Waves. Split Arc. Computed.

very pronounced jog at the beginning and end of each alternation; it may be taken as typical of the "gaseous conduction" referred to above, and agrees fairly closely with the equation $e = i^2/4{,}000$. Thus during gaseous conduction the voltage is proportional to the square of the current and

$$e = i^2/a \tag{5}$$

where e and i are the *instantaneous* values of the current and voltage over the arc and a is a constant.

In the oscillogram, Fig. 4, "gaseous conduction" may be assumed during the first and last part of each alternation, that is, while the voltage is below that necessary to establish an arc. These parts of the curve, like the whole of Fig. 5, are in fair agreement with equation (1). Using the same value of the constant, namely, $a = 4{,}000$, Fig. 7 was computed from equation (1) up to 24 v., and may be compared with the actual oscillogram in Fig. 4.

Any similar computation in which the constant a is given a value greater than zero will result in a wave form that has a jog in the voltage wave. An absence of jog in the voltage wave would therefore indicate that a was practically zero and that there was no appreciable gaseous conduction.

The value of a while constant for an alternation, and therefore in a sense independent of the current, nevertheless changes gradually when other factors, themselves dependent on the cur-

rent and the duration of the arc, are varied. Thus an oscillogram taken 5 min. after turning on the current (600 amp.) showed no jog in the voltage line, while in one taken 10 min. later the jog was as pronounced as that in Fig. 4. The absence of jog signifies $\alpha = 0$, so that although the r. m. s. current remained unaltered, α rose from 0 to 4,000 in 15,000 cycles. Examination of our other oscillograms confirms the conclusion that α increases with the duration of the run, and that for a given duration the jog is less with low than with high currents. Hence α must increase at least as rapidly as the square of the r. m. s. current.

The oscillogram redrawn in Fig. 6 shows an intermediate stage between the purely gaseous conduction of Fig. 5 and the steady a. c. arc. Each alternation begins with the form of curve characteristic of gaseous conduction, but the voltage rises to 60 v. instead of the 28 v. of the stationary a. c. arc; something then occurs, possibly the passage of a spark, and the potential difference over the carbons falls to 3 or 4 v., rises again, falls, and so on.

More thorough study of these intermediate stages should do much to clear up the mechanism of arc conduction; the passage from the smooth curve of Fig. 5 through the hills of Fig. 6 and the saw of Fig. 4 to an almost smooth topped wave must in the end be linked causally with the cooling of the electrodes, the dissipation of the gases, the loss of conductance and, perhaps, with traces of impurities scattered through the electrodes. Of these the thermal effect of the current seems the least important, while some other effect—ionization perhaps—consequent on its passage is the most. For instance, if we compare a silent a. c. arc with a split arc of the same length, the amount of heat per second and therefore the temperature of the silent arc is lower, and we would expect its voltage to be the higher whereas experiment shows that the reverse is true.

METHOD OF COMPUTATION.

In the following discussion the symbols v, e, R, and i are used to denote the instantaneous line voltage (over both rheostat and arc), the instantaneous arc voltage, the resistance of the series rheostat, and the instantaneous current, respectively.

Since the arc and rheostat were connected in series, and the circuit was practically non-inductive, the equation

$$v = e + i\,R \tag{6}$$

will always hold. In our work the line voltage was a sine wave and had the constant r. m. s. value of 125 volts (that is, maximum instantaneous value = 177 v.), therefore

$$177 \sin \theta = e + i\,R \tag{7}$$

where $\theta = 2\pi ft$, f being the frequency and t the time.

The relation between voltage and current during gaseous conduction (see page 215) is given by

$$e = i^2/a \tag{5}$$

combining (5) and (7) there results

$$177 \sin \theta = i\,R + i^2/a \tag{8}$$

and

$$177 \sin \theta = e + R\sqrt{a\,e}. \tag{9}$$

Using (8) and (9) and the appropriate voltage-arc length relation, graphs such as Fig. 7 can be constructed.

Graphical Method. We have found the abacus shown in Fig. 8 a great convenience in making computations, such as are needed for the construction of Fig. 7.

In the abacus the ordinates represent values of e and the abscissæ values of i. The scale of e along the perpendicular axis is also used as a scale of $v = 177 \sin \theta$. The line AB is drawn to give the constant voltage corresponding to equation (2) or equation (4) as the case may be, and the curve OMP is drawn to represent equation (5). Then if OX represents v and XZ makes an angle $a = \tan.^{-}R$ with the horizontal line XY, the co-ordinates of the point of intersection of XZ with AB give the values of e and i corresponding to equation (2) (or equation (4)); and the co-ordinates of the point of intersection of XZ with OMP the values of e and i, corresponding to the equations (8) and (9). Thus if a parallel ruler be set on the line XZ and moved so as to cut the perpendicular scale at different values of v (tabulated from a table of sines), corresponding values of

e and i can be read from the chart; plotted against θ they give the wave forms corresponding to the equations used in drawing AB and OMP. In the abacus shown in Fig. 8, AB is drawn for a 6 mm. split arc OMP for $a = 4{,}000$, XZ for the resistance used when the oscillogram shown in Fig. 4 was made, and XT for the resistance used when the oscillogram shown in Fig. 5 was made, while OX represents the value of v when $\theta = 90°$.

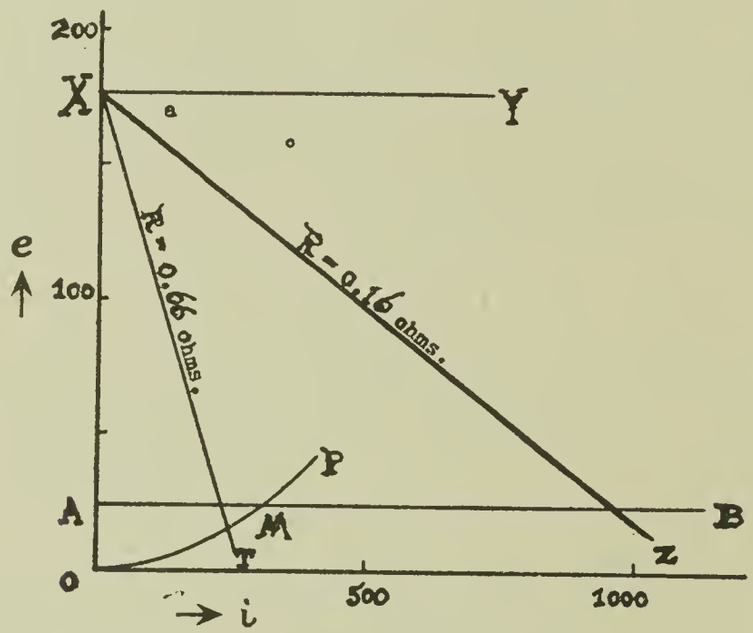


FIG. 8. Abacus for calculating the wave forms of voltage and current.

MECHANISM OF GASEOUS CONDUCTION.

A hypothetical mechanism that would result in an equation such as (5) can be described as follows:

Let us suppose that at any instant n particles each carrying a charge c are moving across a gap of length L with a velocity s, then

$$i = ncs/L \tag{10}$$

The kinetic energy of each particle would be $0.5\ ms^2$ where m is the mass of each particle. The work done on each particle would be ec where e is the voltage over the gap. Equating these we get

$$0.5\ ms^2 = ec \text{ and } s = \sqrt{2e\ c/m}. \tag{11}$$

Therefore $$i = ncs/L = (nc/L)\sqrt{2e\ c/m}. \tag{12}$$

or $$e = i^2/a \tag{5}$$

where $\alpha = 2n^2c^3/L^2m$. The assumption of a constant α would on this supposition involve mainly the assumption of a constant n.

SUMMARY.

Two distinct types of a. c. arcs (split arcs and silent arcs) are described; the voltage over a silent arc is the same as that found for a d. c. arc of the same length (that is, $= 0.99L$), and the corresponding voltage over a split arc is about 18 volts higher.

Voltage and current wave forms of a split arc, before and after a sudden increase in the external resistance, are shown; and an equation for "gaseous conduction," and an explanation of the temporary drop in voltage immediately following such a change are developed. An oscillogram showing an "intermediate stage" in the recovery of the voltage after a drop produced in this way suggests further studies, that should help to elucidate the mechanism of arc conduction.

A graphical method is given for calculating the wave forms of voltage and current, from the characteristics of arc and gaseous conduction and the electrical constants of the circuit.

A simple mechanism of gaseous conduction is outlined that is in accord with the equation we have developed from our oscillograms.

These experiments were carried out in the Electrochemical Laboratories of the University of Toronto during the winter of 1923-24; the writers are indebted to Professor W. Lash Miller for the interest he has taken in the work, and to A. R. Gordon for his help in making the oscillograms.

DISCUSSION.

J. KELLEHER[7]: I do not think we appreciate the importance of this work that Mr. Westman has been conducting for the last three years. It is a theoretical attack on a very practical subject, regulating furnaces up to 50 tons capacity, as we have seen in the Ford plant, and in some cases of connected loads of 20,000 kilowatts. It was due to the difficulty of regulating arc furnaces that this work was commenced. Mr. Westman, in the wiring diagram you

[7] Electrical Engr., FitzGerald Labs., Niagara Falls, N. Y.

show a d. c. ammeter. I would like to know if direct current was observed emanating from the arc? I should think that if you have 200-ohm shunts across the arc, as shown, you would get no direct current, due to the e. m. f. of the arc, because the ammeter shunt is outside the arc circuit.

Another thing: The current oscillograph strip is also connected outside the shunts, which would alter the wave form of the current considerably. Going now to the oscillographs on page 214, it would be interesting to know which was the cathode on the first half of the cycle shown and which was the anode, because there is considerable discrepancy between the amplitudes of the voltage waves, and a slight discrepancy in the amplitudes of the current waves; also it would be interesting to know if the energy in each half cycle is the same, because according to these oscillographs the energy will probably be smaller in one case than in another. If this is due to the fact that in one case the anode is on the top and the cathode is on the bottom of the furnace, it is a thing that might be investigated. If this is the fact, would a horizontal arc, such as is used in the Detroit brass furnace, have equal amplitude for voltage and current waves? If not, then the theoretical oscillogram shown in Fig. 7 is incorrect. When running one of these arcs, was a noticeable periodicity of wave distortion observed? In my own work on arcs in a small furnace every 8 1/3 cycles (this was a 25-cycle furnace) the wave forms were very badly distorted, and then after a period of 8 1/3 cycles the wave form became more or less uniform. It almost seemed as though there was a sub-period, that is, one-third of the fundamental period of the supplied current present in the furnace, due to some peculiar action of the furnace. I must state though that this was not done between carbon or graphite electrodes,, but between an arc playing upon a basic slag, comparable to a steel furnace slag.

A. E. R. Westman: The shunts connected across the arc as shown in Fig. 1 have so high a resistance as compared to the apparent resistance of the arc, or the combined resistance of the series rheostat and the primary of the transformer, that their introduction does not affect appreciably the readings of the meters or the wave forms of the oscillograms.

While, as Mr. Kelleher points out, Fig. 4 indicates some rectification in the arc, this is not true for most of our oscillograms and is due to some slight unsteadiness in the arc, which is not due to the vertical orientation of the electrodes.

None of our oscillograms show any periodicity such as Mr. Kelleher has found, and as his experiments differed from ours in that he had slag and molten metal present. The periodicity he found might be due to some periodic disturbance in the bath.

We do not claim that the data presented in this paper are directly applicable to such cases as that of the Detroit brass furnace, cited by Mr. Kelleher, where considerable zinc vapor is present. However, the same method of attack can be used in investigating such cases, and Mr. Walker, the co-author of this paper, intends to make quantitative measurements of the effect of silica and zinc vapors on the a. c. arc.

J. Kelleher: I would like to state that during the time that the oscillograph was connected to our furnace, over a period of 25 seconds on a slow film, the arc was under constant observation,[8] and when the oscillograms were being taken the slag was perfectly flat and normal.

[8] See my paper, Trans. Am. Electrochem. Soc., 38, 309 (1920).

An address by the Chairman of the Symposium on Corrosion, presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 2, 1924.

INTRODUCTION TO SYMPOSIUM ON CORROSION

By B. D. Saklatwalla.

Everybody is well acquainted with the subject of corrosion and its importance, and any remarks that we may make would be more or less superfluous. However, in regard to this symposium, I have heard several ask as to why the Electrochemical Society should sponsor the subject of corrosion. In my opinion the Electrochemical Society is the one most fitted to do this, because, as some of these papers will show you, the question of corrosion seems to be altogether an electrochemical question. The purely chemical side of it is being relinquished. At one time there were two theories in existence, the electrochemical theory and the purely chemical theory, and the sponsors of the chemical theory have weakened considerably.

The purpose of this symposium, as of the several others that have been held on corrosion, is to get some definite line of thought on the whole question. Considerable work has been done on corrosion, but we do not seem to make headway in any well-defined direction. Like most other metallurgical questions, especially in ferrous metallurgy, we seem to be rushing into the complex without first mastering the fundamentals. All work that has been done on a large scale has been, not on the material itself, but, as we might say, on the prevailing conditions. Electrolytic action, protective films or colloids, etc., are all results of conditions under which the material exists. Very little work has been done on the nature of the material itself. One of the papers today will take up that point. My conclusion why we have not worked more on the nature of the material itself is that such experimentation is so extremely difficult to carry out. The condition problems, although they may be complex, are much simpler than the material problems.

Now this particular symposium today is rather interesting, inasmuch as our efforts to get our friends on the other side of the Atlantic to collaborate with us on this problem have been more or less successful. We have obtained several papers from Great Britain from men of recognized authority in this particular work. While the authors are not present to read their papers, we hope that everyone present will do them justice and honor, by freely discussing any of the points that they have brought forth.

A paper presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 2, 1924, Dr. Saklatwalla in the Chair.

FILM PROTECTION AS A FACTOR IN CORROSION

By Frank N. Speller.[2]

Abstract.

It has taken several years of practical experimenting, after the cause of corrosion of iron in closed water systems was understood, to bring the principles of corrosion prevention into practical use. With the mechanical de-aerator and de-activator for removing oxygen, the problem seems to be solved for large closed systems, while the smaller ones, we believe, can be taken care of, to a large extent at least, by the use of film-forming compounds. For small hot-water systems it has been found that a special grade of silicate of soda gives positive results in corrosion prevention. The question of whether or not it is practicable and economical to use *sodium-silicate* on a large scale in cold water supplies remains to be answered, but it seems highly probable that this can be done. With some domestic waters, lime may be used to advantage, if applied with careful control. There seems to be no doubt as to the benefit to be derived from the proper use of protective films in retarding the corrosion of iron, lead, brass and other metals. This should be carefully considered by the technical staff of municipal water works.

The word "film" is used here in the broad sense to include all kinds of natural protective coatings, formed in the process of corrosion, and consisting in whole or in part of the products of corrosion. Although for some time the influence of films in retarding corrosion has been recognized, the importance of its detailed knowledge has only recently been felt.[3]

[1] Manuscript received July 21, 1924.

[2] Metallurgical Engr., National Tube Co., Pittsburgh, Pa.

[3] Speller, J. Franklin Institute, **193**, 519 (1922); Bancroft, Proc. A. S. T. M., **22**, II (1922).

These films can be either solid or liquid. The concentration of ferrous hydrate in solution on the surface of the metal may be considered as a liquid protective film, and has an important influence on the rate of corrosion. It seems highly probable, as Whitman has suggested, that the solubility of $Fe(OH)_2$ in any solution has an important effect on the production of protective films. Preliminary work indicates that a relation exists between this solubility factor and the initial rate of corrosion in solutions of NaCl, Na_2SO_4 and $Na_2Cr_2O_7$.[4]

This discussion, however, refers particularly to solid films. If these are sufficiently porous, so as to permit the solution to penetrate to the metal, and at the same time interfere with the diffusion of oxygen, the area covered by such films becomes anodic, and is likely to suffer rapid corrosion and pitting. Organic matter, porous boiler scale, or similar material in contact with metal, is apt to cause pitting on this account. To be protective, such films must be sufficiently impervious to prevent the solution from coming in contact with the metal, or at least to prevent circulation of the solution and the diffusion of oxygen to and from the surface of the metal.

CLASSIFICATION OF CORROSION FACTORS.

It may be useful to consider for a few minutes the relation of film protection to other corrosion factors. For our purpose it is convenient to classify the main factors influencing corrosion as follows:

Primary factors.

(Essential to initial corrosion)

Solution potential of the metal	anodic reaction
Concentration of metal ions in solution.....	
H-ion concentration of solution in contact with metal.....	cathodic reaction
Rate of H removal (a) by evolution as gas (b) by oxidation	

Secondary factors

(Affecting ultimate rate of corrosion)

Film protection, overvoltage, composition.

Velocity, temp., oxygen solubility and rate at which oxygen reaches metal.

Dissimilar metals in contact, concentration cells.

Humidity of air, depth of immersion, viscosity of solution and about 30 others.

[4] Private communication from the Laboratory of the Mass. Inst. of Technology.

While in this system of classification film protection is properly placed among the secondary factors, it is obvious that in many cases this may ultimately become the controlling factor determining the rate of corrosion.

NATURAL PROTECTIVE COATINGS.

It has been difficult to understand why the same kind of metal, although exposed to apparently identical conditions, lasts in some localities so much longer than in others. Differences in composition of the metal and in the corrosive character of the environment do not always afford sufficient explanation of this experience. As in the human system nature causes certain diseases, and at the same time provides protection, so does she also promote corrosion of metals and often provides a considerable amount of natural protection. This protection appears in various forms.

Natural Protective Coatings Formed in Water.

The wide variations in the rate of corrosion of both wrought iron and steel water pipes in different localities is well known, and especially marked in the case of hot water supply lines of buildings. For example, under the same conditions of service a galvanized iron hot water pipe may last ten years in New York, and perhaps twenty in Chicago, and probably thirty in some other locality without developing any defects due to corrosion. Variations in the *initial* rate of corrosion by different waters is slight, and not sufficient to explain these facts. From examination of many samples of corroded pipe from different localities it appears that the cause of this difference is mainly due to the difference in degree of formation of a protective scale by the water. Naturally, the purer the water, the less chance there is of forming a protective coating of this kind, although rust (precipitated iron hydroxide) alone exerts more or less of a protective influence. Organic material and fine sediment carried in suspension and distributed with a fair degree of uniformity over the inside surface of the pipe by adsorption sometimes afford considerable protection.* In pipe carrying some western waters the author has seen such sedimentary coatings 3.2 mm. (0.125 in.) thick. Apparently corrosion from the very pure

* The same phenomenon is referred to in detail by J. N. Friend, D. W. Hammond, G. W. Trobridge, "The Influence of Emulsoids Upon the Rate of Solution of Iron." This volume, page 283.

waters in certain localities (such as New England) has increased since filtration plants have come into more general use.[5]

A gelatinous protective film consisting mostly of silica is occasionally found in water pipe. This is thought to be of bacterial origin, as it is intermittent in formation and (according to Baylis[6]) seems to be associated with the presence of certain bacteria in the water at certain times. It is possible that this film is the result of reaction between (positive) colloidal iron hydroxides and (negative) silicic acid.

Calcium carbonate undoubtedly plays a large part in the protection of metal from corrosion according to the relation of the amount present to the free carbonic acid content of the water. Certain waters may be more corrosive at some seasons, due to the removal of carbonate scale by a temporary excess of free CO_2 in the water.

Many samples of rust and scale from the inside of water pipes which have shown great durability have been found to contain carbonate of lime and silica, forming a fairly durable protective coating. The silicates seem to be of especial importance with respect to the permanence of these protective films. In the region of the Great Lakes, and in some other localities, the water forms this carbonate scale so rapidly that in the course of a few years the inside diameter of small pipes may be reduced to as much as one-half. This scale forms in both hot and cold water lines, but more rapidly in the former. Naturally such pipes will show very little corrosion. The following are typical analyses of scale from water pipes in Great Lakes cities:

From	Iron Per cent	Lime Per cent	Silica Per cent
Detroit, Mich. (galv. pipe)	28.4	3.0	4.8
Chicago, Ill. (galv. pipe)	9.65	1.74	4.40

On the other hand, analyses of scale from pipe in Pittsburgh, Pa., where the water is considerably more corrosive, show much greater amounts of iron (rust) in proportion to the lime and silica.

From	Iron Per cent	Lime Per cent	Silica Per cent
Pittsburgh, Pa. (galv. pipe)	54.55	1.91	3.06

[5] Discussion by M. F. Newman, Mgr., Water Purifying Department, Wm. B. Scaife and Sons Co., Oakmont, Pa., of paper on "Water Deactivation," by the author; see also Donaldson, Jour. Am. Water Works Assoc., **11**, 653 (1924).

[6] Private communication.

The same kind of film protection plays a part in steam boiler practice. If the water does not form films or scales, it is desirable to keep the oxygen content of the water under 0.5 cc. per L., but if the water deposits scale its somewhat higher oxygen contents will remain harmless. For this reason power plant engineers often prefer a little scale, and a certain amount of lime is recommended in filling a new boiler.

Thresh[7] describes a recent investigation which he made on corrosion of lead pipe by certain waters in England. Results of analyses of quite a number of domestic waters indicated that, as a rule, a low rate of lead solution was associated with relatively high silica and high alkalinity in the water. Tests which he made on waters after the addition of about 10 p.p.m. sodium silicate showed that there was practically no action on lead, and also that the treated water was clearer in color after passing through iron pipe than would be the case with the same water before treatment.[8] Silicate addition to domestic water supplies is being tried on quite a large scale in one of the large cities in England. The results may be of considerable importance, especially in small plants, provided this treatment does not prove to be too costly. There may be a considerable reduction in the silica in solution as the water flows through the mains, which would then prevent the treatment being effective throughout the system. This has been found to be the case where such treatment has been tried in some large hot water systems.

Natural Protective Coating Formed in Air.

Some metals, such as zinc, aluminum, nickel and copper, form a more or less protective oxide in air which retards further corrosion. Iron carrying a small amount of copper, when exposed to the atmosphere in certain localities, forms a dense, hard layer of rust, which seems to have much to do with the relatively high resistance of copper-bearing iron to atmospheric corrosion. In 1908 the author, in examining some French steels, which had been left on the Isthmus of Panama since 1888, found many instances where pipe which had not been protected in any way by artificial coatings was in excellent condition, having apparently acquired a

[7] Notes on the so-called action of water on lead, Analyst, **46**, 270-279 (1921).
[8] Donaldson, J. Am. Water Works Assoc., **11**, 556 (1924).

natural film of oxide. This oxide was probably formed during the dry season. Samples of this pipe which were machined free from scale rusted badly in a few months like the more modern metal. Seemingly, the ultimate life of iron depends considerably upon the conditions under which it is first exposed, which determines whether or not a permanent protective coating will be formed.

The well-known case of the Delhi iron pillar erected 1600 years ago in Hindustan, and which is today practically uncorroded, is probably due to the forge scale which was hammered into the metal in the course of fabrication. The longevity of life of this iron has also been favored materially, of course, by the dry climate. Samples of old wrought iron forged articles have been found in a good state of preservation by Dr. W. H. Walker and the author. However, on filing off some of the scale which was invariably found on the surface of these specimens and exposing them to the weather, the underlying metal rusted rapidly at the exposed places.

Natural Protective Coatings Formed Underground.

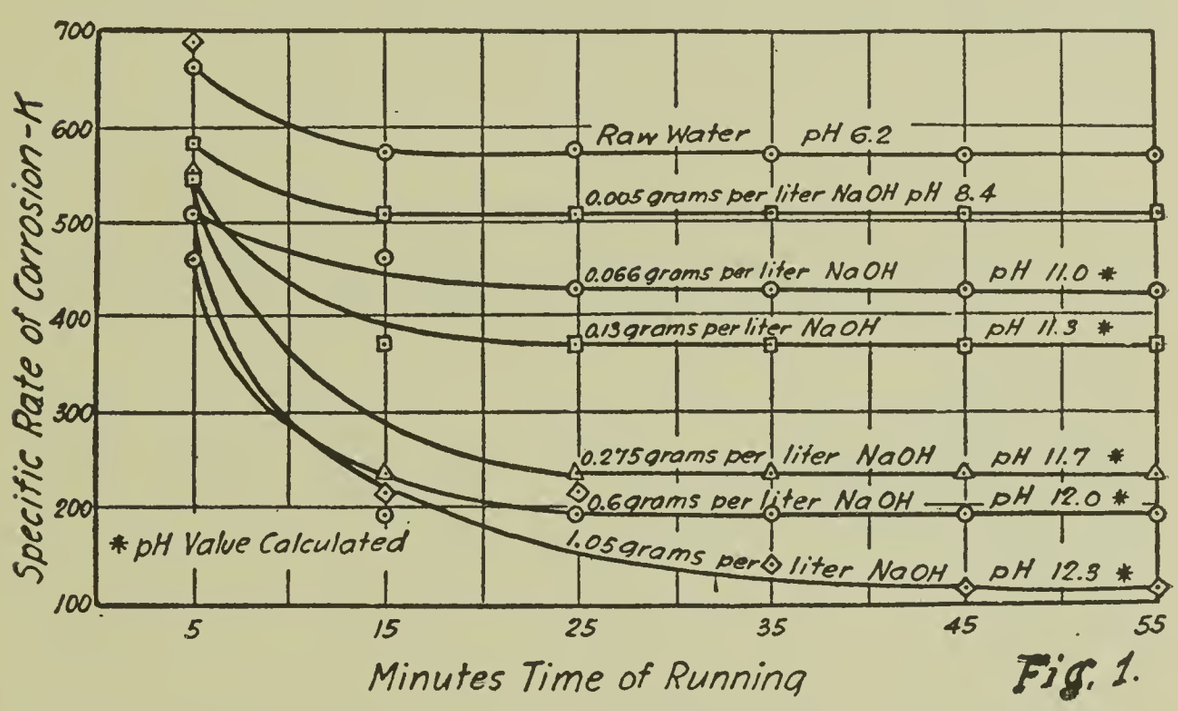
Certain kinds of clay and other soil formations have the property of producing mixtures with iron rust, which form hard, impervious coatings on the surface of pipe buried in the soil. These coatings in a large measure protect iron from further corrosion. This condition is sometimes found on gas and water mains which have been buried in such soil for a number of years, and should therefore be left undisturbed if possible.

FACTORS INFLUENCING THE CHARACTER AND DEPOSITION OF PROTECTIVE FILMS IN WATER.

As principal factors may be designated the H-ion concentration and the composition of the water, particularly its less soluble constituents. The solubility of ferrous hydroxide is also probably an important factor. It seems highly probable, as suggested by Bancroft, that film formation may be studied to best advantage from the standpoint of colloidal chemistry.

When the metal is continuously immersed in the water, other things being equal, the pH value is the controlling factor in film formation. It has been shown that the effect of alkalinity on

corrosion is due to the rapid formation of a protective layer of hydroxides of iron upon the metal surface. As a matter of fact, in a series of tests using the differential (oxygen-drop) method of testing, the results indicated that the initial rate of corrosion in the first few minutes of contact of metal with the solution is practically the same, independent of the alkalinity.[9] After a short time the rate drops to a minimum depending on the alkalinity, after equilibrium has been established between the contending forces. (See Fig. 1.)



Specific Rate of Corrosion *vs.* Time of Running. With various concentrations of NaOH. 0.5 in. (1.3 cm.) steel pipe; 150° F. (66° C.) Pittsburgh city water.

ARTIFICIAL PROTECTIVE COATINGS FORMED IN WATER.

In experiments on a large scale on the removal of oxygen by deactivation as described by the author,[10] it has been found that the rate of corrosion decreases about 30 per cent in a year with some waters, due to adhering scale and rust precipitated on the surface of the metal.

The solubility of $CaCO_3$ in water varies with the pH value, due to the CO_2 content of the water, and the percentage of other soluble salts present. This relation has been worked out experimentally and charted by J. R. Baylis.[11] Water with a pH

[9] Ind. Eng. Chem., 16, 395, Fig. 5 (1924).

[10] J. Franklin Inst., 193, 515 (1922).

[11] Chemist, Filtration Department, Water Works, City of Baltimore, Md. Private communication.

value on or above the equilibrium curve in these diagrams will deposit a $CaCO_3$ scale, while below the curve no scale will be found. This principle has been used in the control of water treatment with apparent success at the Water Works, City of Baltimore, Md., where the pH of the water after filtration is raised from 6.5 to 8.2 by the addition of about 10 p.p.m. of $Ca(OH)_2$. Mr. Baylis reports that this has been sufficient to reduce corrosion and red water to a negligible quantity. It takes a few months to build up such a protective film with lime, and the excess hardness produced might be objectionable. This objection does not apply to the use of sodium silicate for this purpose.

TABLE I.

Analyses of Artificial Protective Scale in Iron Pipe.

Location	Iron Per cent	Lime Per cent	Silica Per cent	Magnesia Per cent	Zinc Per cent
Pittsburgh, Pa.					
Westinghouse Cafeteria.....	2.8	....	30.08	.....	21.10
Mellon Institute Supply Line..	23.4	0.64	28.64	16.89	0.77
Mellon Institute Return Line..	46.3	0.56	9.20	.....	....
City water softened to zero hardness	54.43	0.06	4.62	2.12	.....
McKeesport, Pa.					
Y. M. C. A.....	3.5	3.9	12.72	.....	28.90
Ellwood City, Pa.					
Club House	25.20	1.50	13.00	4.21	.....

In the Baltimore system it is reported that they find very little drop in oxygen in the mains, even after the water has made a complete circuit which requires 20 hours.[12] This principle might be used to advantage more generally in the control of corrosion in municipal water systems.

Observations in the study of corrosion of steel pipe by water in different localities, referred to above, led the author to design some experiments in 1920, by which the action of soluble silicates in water could be investigated. The rapid oxygen-drop method of determining the rate of corrosion was designed mainly for this purpose and has been found very useful in such investiga-

[12] Private communication.

tions.[13] This apparatus (see Fig. 2) consists of a definite length of uncoated iron pipe, through which the water being tested is passed at a fixed rate of flow at a constant and definite temperature. The decrease in the oxygen concentration of the water, in passing through the pipe, indicates the rate of corrosion at any time. This rate of corrosion is largely controlled by the surface films on the pipe.

Liquid sodium silicate has been used as the essential basis of proprietary compounds for use in domestic hot water systems to form a protective scale on the inside of the pipes. When added to water in small quantities this compound is usually broken up by hydrolysis into SiO_2 and NaOH. The colloidal SiO_2, being precipitated with ferric hydroxide, builds up a dense and adherent film of high corrosion resistance.

The protective nature of such films or scales is probably improved by the formation of a mixture of insoluble hydroxides of iron or other metals, with silica or silicates and calcium carbonate, when these are present. While such coatings are, no doubt, more or less porous in character, they serve to retain a high concentration of metal ions near the metal, and to interfere with the diffusion of oxygen and other corroding agencies to the metal, thereby retarding corrosion. If the film is not continuous or the treatment is intermittent, pitting may result. The good results obtained by the use of silicate films in protecting pipe from corrosion illustrate an important practical application of this principle. This investigation also indicated the manner in which these "self-healing" films may be formed and maintained in practice. Some analyses of protective scale artificially produced by addition of soluble silicates are recorded in Table I.

Curve 2, Fig. 3, illustrates the quick drop in rate of corrosion using Pittsburgh water when charged with sodium silicate (15 p.p.m. has been found to be sufficient with most waters). Curve 1 on the same chart shows the amount of corrosion with water from the same supply, without silicate addition.

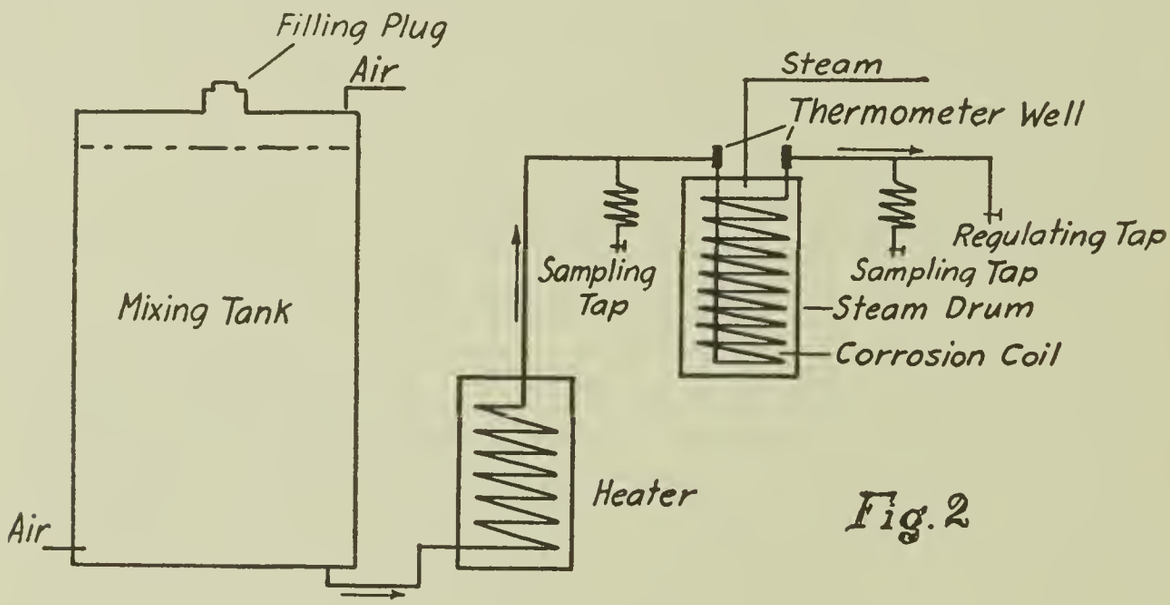
In order to investigate fully the use of silicates as a protective measure against the corrosion of water pipes, these preliminary experiments were followed in 1922 by some more detailed investigations on the properties of these films and the best means of

[13] Ind. Eng. Chem., 16, 393 (1924).

application of this treatment in practice. The experimental details of this work were carried out by C. R. Texter at Mellon Institute of Industrial Research, Pittsburgh, Pa., and by R. P. Russell at the Research Laboratory of Massachusetts Institute of Technology, with the financial support of the National Tube Company and with the co-operation of the author.

The results of these investigations indicate:

1. That silicate of soda has a marked effect on the rate of corrosion of iron in hot water, and a distinct but lesser effect on corrosion in cold water, without entirely stopping corrosion. The



Corrosion Testing Apparatus.

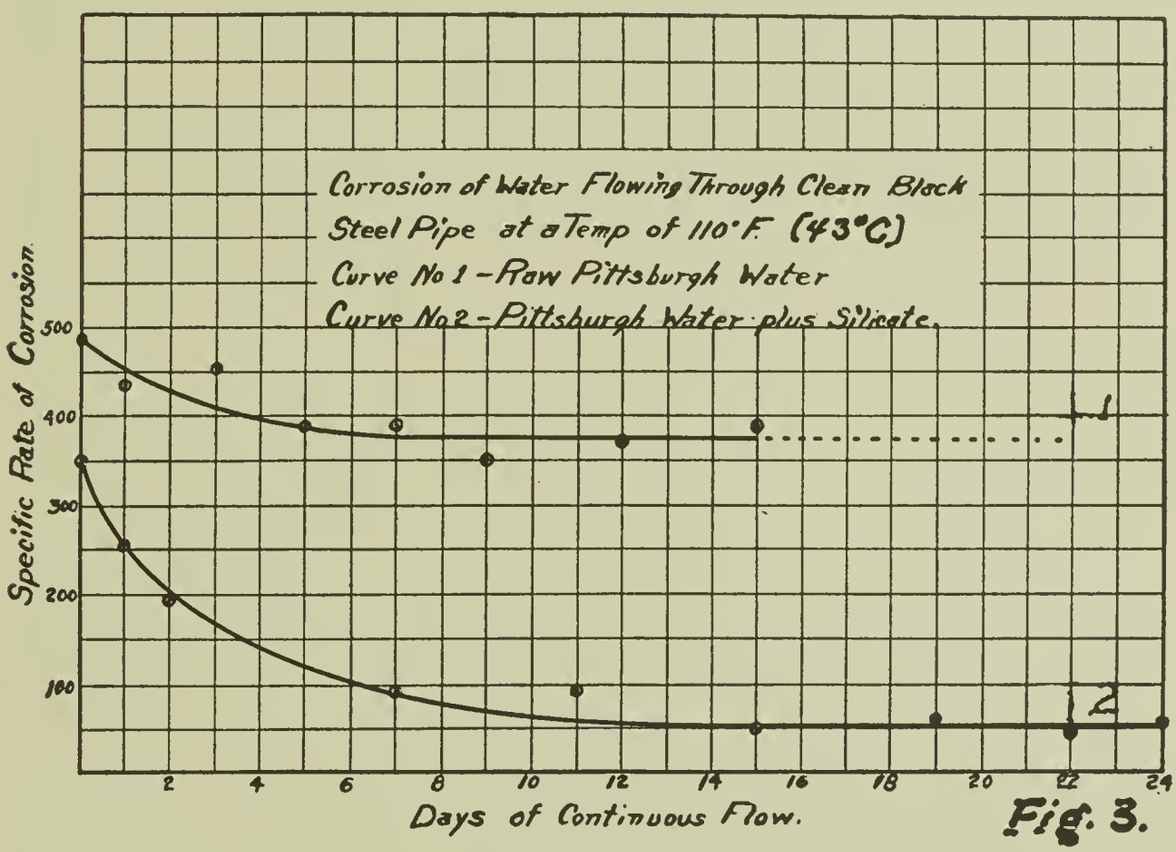
specific protection depends to some extent on the presence of other scale forming matter in the water, although protective films are formed with the use of sodium silicate in water even of zero hardness rendered so by the Zeolite treatment.

2. That the amount of silicate required is about 15 p.p.m. for the first application. After a substantial protective film is formed a concentration of 5-10 p.p.m. is usually sufficient to maintain the film in hot water pipes.

3. That anhydrous sodium silicate having 3.25 SiO_2 and 1 Na_2O is best for use with *hot* water, as it is less soluble than the more alkaline silicates of soda. In no case, however, will all the silicate be dissolved. Sodium silicate in solid form is preferable to the liquid, because the supply requires refilling only every 2 to 4 months, whereas the liquid addition should be made every day

or two. Automatic feed devices for liquid additions where the rate of water consumption varies considerably in short intervals have been found to be unreliable.

The addition of sodium silicate should be especially useful in laundries, where it not only tends to keep the water clear and adds considerably to the life of the system, but also softens the water with some economy of soap.



Corrosion of Steel Pipe by Pittsburgh water.

In domestic use the addition of too much sodium silicate may give unpleasant results, when the water is used in cooking, because of excessive alkalinity. The results of careless application would be manifested first by the water becoming decidedly soft to the hands before the concentration was high enough to affect the human system. With a little attention and experience it is believed that the use of this treatment can be easily controlled with considerable benefit to those using corrosive waters. As "rusty" water is very objectionable in domestic use, the addition of soluble silicates ought to help materially in overcoming the so-called "red water plague."

LIMITATION OF SCALE PROTECTION ON WATER PIPE.

When the cost is not prohibitive, it is naturally best to remove the source of the trouble, which in water corrosion is usually the dissolved oxygen. This has proved to be economical and effective after several years of practical trial in a large number of installations. However, for residences of average size and smaller, the cost of deoxygenating water is at present prohibitive to so many that the best solution of the problem in such cases would seem to be to give the water the necessary amount of silicates to form on the metal a self-healing protective film.

In hot water systems the silica is deposited more densely near the source of supply, and does not form a protective scale much more than 100 to 200 ft. away from the point of application. Furthermore, if the protection is not extended throughout the entire system, or maintained, it is evident that the part unprotected will be subject to more severe attack, due to the higher concentration of oxygen in the water. This fact has been proved by observations upon the use of silicate in two large buildings in Pittsburgh, and indicates that such treatment should not be applied to systems having lines (in any case) over two hundred feet in length. Of course, the silicate might be added at more than one point, but the increased attention and apparatus required would usually be objectionable.

The addition of silicates to cold water reduces corrosion about 50 per cent, according to the tests in Cambridge, Mass.,[14] whereas in hot water a film was built up in 30 days which gave a reduction in corrosion amounting to 80 per cent, as measured by the difference in oxygen concentration in water flowing through the system. It is probable that this treatment will carry farther with cold water, perhaps sufficiently to treat the water of a large system (on a large scale), as is now being tried in England. *The alkaline silicate with a ratio of Na_2O to SiO_2 of 1 to 2.25 has been found best for cold water.* When sodium silicate is added to cold water it seems to be necessary to use it in liquid form, since the solid form becomes coated with an insoluble film, and as a consequence does not go into solution completely.

Any system of water treatment requiring the addition of re-

[14] Report from Research Laboratory of Applied Chemistry, Mass. Inst. Tech., Cambridge, Mass.

agents involves practical difficulties in controlling the amount of such additions. The silicate treatment, however, does not need to be continuous, and apparently may be omitted entirely for a few days without bad results after a substantial film has been formed. Proprietary compounds, consisting essentially of sodium silicate, have resulted in failure in some cases probably due to improper application and to the attempt to use the treatment in too extensive hot water systems to which it was not adapted and would do little good. In fact, in large systems such compounds may be harmful for reasons given above.

The need and use of scale protection should be anticipated before the piping system becomes badly coated with rough tubercles of rust, which may reduce the capacity of the pipes 50 per cent or more.

DISCUSSION.

O. P. WATTS[15]: Was this treatment carried out in Baltimore, a sodium silicate one?

F. N. SPELLER: No, that was a lime treatment, but that was a matter of economy. The disadvantage of lime is that you harden the water slightly. It may cost too much to use sodium silicate, but, as I have mentioned, Dr. Thresh in England has tried out the use of sodium silicate in municipal supplies and is now making a large scale experiment along that line in Birmingham, from which we may expect some results. The preliminary tests have shown a large reduction in the rate of corrosion in both lead and iron pipes, and this treatment has entirely cleared up the water. That is a factor that worried people more than the corrosion, the so-called "red water plague."

COLIN G. FINK[16]: I am glad to see Mr. Speller favor the film theory, although I know he has been a great exponent of de-aeration in the past. I have always had a lot of faith in that film theory. I think Mr. Speller would do well now to get a physically active film, a film which will take care of the oxygen in the water, and dispose of that somehow or other. This is not a hypothetical

[15] Assoc. Prof. of Chem. Eng., Univ. of Wisconsin, Madison, Wis.
[16] Head, Division of Electrochemistry, Columbia Univ., New York City.

idea. We have actually worked out this principle in the case of insoluble anodes.

LOUIS KAHLENBERG[17]: In the midst of the many theories of corrosion, it is gratifying that Mr. Speller has approached the problem from a practical standpoint. Some years ago there was reported to me from St. Louis a case of corrosion of refrigerator tubes, through which they were pumping calcium chloride brine. On inspection it was found that the calcium chloride used contained appreciable amounts of magnesium chloride, and that when the latter was not present in the brine the corrosion ceased. Magnesium salts, unlike calcium salts, are prone to form basic salts. This is particularly the case with magnesium chloride. Upon this fact, too, is based the magnesium oxychloride cement, for example. The fact that magnesium salts form basic compounds is of importance in corrosion. Formation of such basic magnesium salts can be shown as a lecture experiment by dipping bright magnesium ribbon into a solution of neutral magnesium chloride. Hydrogen is rapidly evolved, the solution becomes alkaline to litmus and a precipitate of basic salts finally forms.[18]

COLIN G. FINK: Prof. Kahlenberg, you have seen this new table salt which runs so nicely out of the shaker, and you know what was added to that, don't you?

LOUIS KAHLENBERG: They add a number of things—starch or other inert materials, for example.

COLIN G. FINK: The regular thing that they add now is a magnesium salt.

W. D. RICHARDSON[19]: With regard to Dr. Fink's statement of the addition of magnesium salt to sodium chloride to make it run smoothly, I think, although I am not precisely informed, that "magnesium salt" is too broad a term. I have heard what they actually add is magnesium oxide or carbonate, which is quite a different matter.

COLIN G. FINK: Is it a question whether oxide of magnesium is a magnesium salt?

[17] Prof. of Chemistry, Univ. of Wisconsin, Madison, Wis.

[18] L. Kahlenberg, Action of Metallic Magnesium upon Aqueous Solutions, Trans. Wis. Acad. Science, **24**, 299 (1903).

[19] Chief Chemist, Swift and Company, Chicago, Ill.

JAMES WITHROW[20]: I would not want to contradict Prof. Kahlenberg's conclusions, but we all must recognize that we frequently obtain a result based upon an idea or theory which we later find entirely wrong, but our work solved the problem at the time. I wonder whether this hydrolysis of magnesium chloride takes place at such a low temperature as we have in the brine system. The effect may be a purely solvent action also. I also had this problem in a refrigeration case in St. Louis. They were really more worried about the fact that these calcium chlorides which contained magnesium chloride also contained bromine, and they blamed their troubles (the flavor of the beer was affected) on the brine. This seemed improbable. As a matter of fact, a great deal of mixed calcium and magnesium chloride is sold and used for brine-refrigeration purposes. The corrosion problem is apparently not serious. We are well aware of the fact that those chemical corporations who sell relatively pure calcium chloride have always used that as a selling point, namely, that magnesium chloride has an effect on corrosion.

F. J. HAMBLY[21]: I wish to express my appreciation of Mr. Speller's paper, and to suggest that it would now be useful to collect and collate the information already published in reference to films which *accelerate* corrosion. Mr. Speller clearly states in his introduction: "The word 'film' is used here in the broad sense to include all kinds of natural protective coatings," though on the following page a passing reference is made to porous films which promote corrosion.

The protective film is the one in which we are naturally most interested, and a study and classification of films showing the conditions under which they prevent, diminish or accelerate corrosion would probably afford useful suggestions for further advances along the lines described in Mr. Speller's valuable paper.

R. J. MCKAY[22]: Mr. Speller pointed out in the first part of the paper that the reason that much of the discussion and work on corrosion has not been constructive has been the attempt to draw too general conclusions from data which were originally insufficient. It is rather an interesting commentary on the methods of

[20] Prof. Industrial Chem., Ohio State Univ., Columbus, Ohio.
[21] Mgr., Electric Reduction Co., Ltd., Buckingham, Que., Canada.
[22] Supt. of Technical Service, International Nickel Co., New York City.

some of our pure scientists that Mr. Speller, in tackling the job more from a practical standpoint, has had to classify the factors of corrosion, and point out that when we are studying films, for instance, we are studying only one factor. The title of the paper is useful as an illustration of his method, "Film Protection as a Factor in Corrosion." In other words, films are not discussed as a panacea or even as most important, but only as one factor, and I believe that if we all adhere to Mr. Speller's method, and realize that most of the specific problems which we attack are merely factors, our work will be more constructive.

A paper presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 2, 1924, Dr. Saklatwalla in the Chair.

THE MICRO-CHEMISTRY OF CORROSION.[1]

By Cecil H. Desch.[2]

Abstract.

The theory of the process of corrosion is still in an unsatisfactory condition. The process is fundamentally electrolytic. Iron rust differs greatly from iron in electrolytic potential. The presence of colloids is not always essential to bring about corrosion. The author has made a microscopical study of the early stages of corrosion. A detailed description of the apparatus employed and of the method of testing alloys is given. Minute traces of foreign substances on the surface of the metal or alloy will often result in entirely different corrosion results. [C. G. F.]

In spite of the great interest that has been taken in the subject of corrosion during recent years, and the large amount of experimental work on the corrosion of metals and alloys, which has been undertaken with the object of finding means of lessening the serious economic losses due to corrosion, the theory of the process remains in a most unsatisfactory condition. It has been clearly shown that no corrosion can occur unless an electrolytic system be present, involving a cathode, an anode, and an electrolyte. The difference of potential necessary for the setting up of such a system may be provided by impurities in the metal, by the presence of two distinct phases in alloys of duplex structure, by contact with other conducting substances, or by local differences in the condition of even a pure metal, as when a locally cold-worked region occurs on a metal softened by annealing.

It is known from such accurate work as that of Lambert[3] that

[1] Manuscript received July 31, 1924.

[2] Professor at the University of Sheffield, England.

[3] B. Lambert, Trans. Chem. Soc., **101**, 2056 (1912) (iron); B. Lambert and H. E. Cullis, *ibid.*, **107**, 210 (1915) (lead).

exceedingly minute differences in the condition of a metallic surface, as of lead highly purified by distillation, will suffice to initiate corrosion. Once the process has begun, the nature of the product of corrosion has a most important influence on the subsequent course of the change. A soluble product is quickly removed, leaving the conditions essentially unchanged, while an insoluble product will affect corrosion in a way which depends on its physical characters. Iron rust, for example, differs greatly from iron in electrolytic potential, and therefore provides an efficient cathode, while it conducts the current fairly well, and by its porosity allows of the accumulation of the products of corrosion when the metal is immersed, or holds the electrolyte in atmospheric rusting. For these reasons, when the rusting of iron has once begun, it continues at an accelerated rate.

On the other hand, aluminum, which from its position in the electrochemical series might be expected to corrode more rapidly than iron, forms a thin tenacious layer of hydroxide, which is almost a non-conductor, and is so impervious as to form a protective varnish, underneath which the metal remains almost unaffected. In tropical climates, where the initial attack is more rapid, these conditions do not hold good, and aluminum vessels become coated with a porous layer, which is not an efficient protection. Aluminum drinking vessels are known to become foul in such circumstances, micro-organisms being retained by the spongy coating, while corrosion gradually proceeds.

The product of corrosion is often colloidal, but the present writer does not regard the attempt of Friend[4] to represent the presence of colloids as essential to corrosion as successful. Either colloidal or crystalline materials may accelerate the process, and the conditions may vary within wide limits.

The initial stages in the process of corrosion are of great importance, as the nature of the product (whether conducting or insulating, electro-positive or electro-negative, porous or impervious) largely determines the subsequent course of the process. For this reason the writer has found it desirable to make a microscopical study of the early stages of corrosion, using small specimens in an electrolyte of definite composition, and controlling the rate by applying a known electromotive force, either by coupling with

[4] J. A. N. Friend, Trans. Chem. Soc., **119**, 932 (1921).

a second metal of known constant potential, or by using an external applied e. m. f.

The apparatus used at first consisted of a stand which would carry a specimen with a horizontal surface of about 2 sq. cm., facing upwards, above which a cathode of platinum gauze of known area was supported in such a way that the vertical distance could be measured on a scale. The electrolyte, the volume of which was 5 cc., was enclosed in a cell built up around the specimen by means of a plastic material, preferably soft wax. When required, by using a deeper cell, a continuous flow of the electrolyte from a burette could be made to pass over the surface of the metal. After definite periods it was easy to remove the plastic wall, wash the specimen, and examine it under the microscope.

This method was used by the writer and S. Whyte in a series of papers,[5] in which the corrosion of various classes of brass in solutions of salts was studied, and it was shown that the corrosion of α-brass in sea water could be exactly imitated by using an applied e. m. f., the microscopic appearances being the same in both cases. Further, the effect produced by the addition of 1 per cent of tin to the alloy, which is known to reduce greatly the amount of corrosion, was explained. In the earliest stages of corrosion, the action of the electrolyte (sodium chloride solution) on the alloy containing tin was actually found to be more rapid than on the simple alloy, but the action was soon checked by the formation of a thin, extremely tough and adherent film of a basic tin salt, which was so impervious as to protect the brass like a varnish.

At the time of the experiments, a new alloy had been introduced for the manufacture of brass condenser tubes, in which 2 per cent of lead replaced the 1 per cent of tin. The action was found to be of a similar character, and it was interesting to observe that when a brass to which only 1 per cent of lead had been added was examined, the basic salt was formed, but was unable to cover the whole surface, remaining in isolated patches, while the addition of 2 per cent provided a continuous protecting layer. The same method was found useful in the study of the corrosion of light aluminum alloys, the difference of potential between the crystals of aluminum or of solid solution and the intercrystalline eutectic

[5] J. Inst. Metals, **10**, 304 (1913); **11**, 235 (1914); **13**, 80 (1915).

being found to localize corrosion, with the production of grooves, which ultimately cause the alloy to disintegrate.[6] A basic salt which does not form an adherent layer may accelerate corrosion, as is seen when copper oxychloride is formed locally, this action having been studied in detail by Bengough.[7]

The apparatus mentioned above did not permit of the continuous observation of a specimen by means of the microscope during the continuance of an experiment, and it was necessary to remove the specimen, wash and dry it, and transfer to the microscope. It has been found that appreciable changes in the surface films of corroded metals may occur during the operations of removing and drying, so that inferences from the appearance of the dried specimen are not always correct. It is therefore desirable to have a means of keeping the surface of the metal under microscopical observation while immersed, and to have means of varying the concentration of the solution, the rate of supply of oxygen and other factors without disturbing the electrical arrangements.

Working in my laboratory, H. H. Beeny has recently used cylindrical specimens of metal, 0.625 in. (16 mm.) in diameter, having one polished plane face uppermost. The cylinder has an axial hole in the lower face, into which a screwed connection may be inserted. All its exposed surface, except for the upper face, is protected with a coating of paraffin wax, so that the anode area is accurately known. As cathode a brass cylindrical vessel, about 3.5 in. (9 cm.) in diameter and 2 in. (5 cm.) deep, is used. The inner cylindrical wall of this vessel is plated with gold, so as to give a cathode of constant area and condition. The specimen is fixed in the center of this vessel, the connecting pin passing through a vulcanite insulating disc.

The whole apparatus is placed on the stage of a metallurgical microscope, the surface of the corroding metal being then central. The anode and cathode may be simply connected by means of a wire or an external e. m. f. may be applied or the current passing may be measured by connecting with a milli-ammeter. A further advantage of this apparatus over the earlier form is that the volume of electrolyte is much larger, so that the estimation of the quantities of metal dissolved is less troublesome, although the

[6] Trans. Faraday Soc., **11**, 198 (1916).

[7] G. D. Bengough, R. M. Jones and R. Pirret, Sixth Report to Corrosion Committee, J. Inst. Metals, **23**, 65 (1920).

quantities to be dealt with are still very small. With the analytical methods now available, difficulties of this kind are not serious.

One lesson which is soon learned when experiments in this direction are made, is the importance of even minute traces of contamination on the surface of the metal. It has been found advisable to clean all specimens after polishing, by making them cathodes in a dilute solution of sulfuric acid with a platinum anode. Traces of grease are most easily removed in this way. When the surface is clean, so that a solution will flow evenly over it, regular results are obtained in the corrosion experiments. It is soon seen that the formation of thin films of gas on the surface, whether of hydrogen or of oxygen, play an important part in the process of corrosion. The electrochemical action may be brought to a standstill by polarization by a film of gas, and this is particularly important when there is no external e. m. f., and the difference of potential is provided by the presence of a second phase, such as cementite in mild steel. The cementite, present as thin lamellæ in pearlite, sets up an electrolytic system with the ferrite, and corrosion would proceed continuously were it not for the fact that the cathode areas may become covered by a layer of hydrogen, and in the absence of any means of removing such a layer the action is arrested. A new action may thus be set up, and the pearlite, being protected, the ferrite areas may be attacked, becoming dark, while the pearlite remains light.

This reversed etching was noticed by Whyte and the writer in steels, and the cause would seem to be as described. Pearlite has such a minute structure that it behaves as a single constituent in etching, and a gas film which is formed upon the cementite seems to cover the whole of the pearlite areas, protecting the ferrite portions of the eutectoid also. This action is not clear; in fact, the whole theory of the influence of one metal on another, worked out for masses of considerable size, needs modification when applied to very finely divided solid phases, such as are found in pearlite or in tempered steels, aged light aluminum alloys, and so forth. The results obtained by H. H. Beeny will be published shortly.

The writer has made no attempt to survey the work which has been done in this field, but has only called attention to the importance of the microscopical study of corrosion. As regards the general theory, he fully accepts the electrochemical view originally

formulated by Faraday, and does not regard water as an electrolyte capable of bringing about corrosion, a substance having a higher electrical conductivity being essential. The recent papers of U. R. Evans contain a statement of modern theory,[8] with which the writer is in general agreement.

The experimental difficulties in the way of any unambiguous determination of the nature of corrosion are intensified by the fact that extraordinary precautions are necessary if experiments are to be made with anything like pure metals. This will be realized when the papers of Lambert, cited above, are studied. Even a minute trace of impurity, such as is always present in commercially pure metals, will suffice to provide the necessary cathode areas, and the labor of providing such highly purified iron and lead as Lambert used, together with the exclusion of impurities from the containing vessels, is very great. Hence it is not surprising that such inconsistent results should be obtained by different workers on corrosion. Even a touch on the surface of a highly purified globule of metal will set up a local difference of potential, so that the specimen under examination is no longer homogeneous. It is to physical laboratories, with their highly perfected technique for working in high *vacua,* and for the elimination of all handling of substances under examination, that we must look for research work on the fundamental characters of corrosion rather than to laboratories fitted for chemical or metallurgical investigations.

University of Sheffield,
Sheffield, England,
July, 1924.

[8] J. Inst. Metals, 30, 239 (1923); Trans. Faraday Soc., 19, 789 (1924).

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THE RELATION BETWEEN TARNISHING AND CORROSION.[1]

By Ulick R. Evans.[2]

Abstract.

Previous work has demonstrated the electrochemical character of many important processes of corrosion; the present paper describes investigations into the attack of gaseous sulfur dioxide on iron and zinc, and that of hydrogen sulfide on copper, with special reference to the part played by water in each case, and also to the essential difference between tarnishing and corrosion proper. Iron and zinc are unattacked by dry sulfur dioxide, but a very small amount of water vapor is sufficient to allow the action to proceed apace. The surface of iron attacked by moist sulfur dioxide is dark, but is covered by tiny, bright circles with a dark spot, apparently a pit, at the center of each. The interior of the pit is probably anodic, and the circular patch around probably owes its brightness to cathodic protection. In some cases, rings of white crystals are seen arranged radially around the pits, evidently representing the corrosion-product.

Dry copper exposed to hydrogen sulfide in the absence of liquid water assumes a series of tints, due to interference, suggesting the direct formation *in situ* of a sulfide-film, in optical contact with the metal. Moisture in very small amount merely stimulates this action, but a film of liquid water, even though very thin and scarcely visible, causes a second type of change, giving rise to a less compact and often non-adherent layer of black or brown sulfide. The zonal phenomena observed in drops of hydrogen sulfide solution placed on a copper surface recall those produced by drops of salt water on iron or copper, and suggest electrochemical action connected with differential aeration. Electric cur-

[1] Manuscript received July 7, 1924.
[2] Cambridge, England.

rents generated between two copper electrodes immersed in hydrogen sulfide solution subjected to differential aeration can actually be demonstrated. The blackening of wet copper by hydrogen sulfide tends to follow the grooves left by emery treatment, the places least accessible to oxygen.

If copper is exposed to moist hydrogen sulfide at a constant temperature, so as to avoid actual condensation of liquid water, the first type of attack may continue until interference tints of the fourth order are reached. The tints are best produced when the hydrogen sulfide is present in small amount, but tend in that case to appear at the bottom or edges of the specimen first, where diffusion proceeds most easily, spreading upward and inward in regular sequence. If, however, liquid water condenses on the specimen at a point to which hydrogen sulfide has still access, the second (electrochemical) type of corrosion is set up, and since the dark product is non-protective, action at that point proceeds apace.

INTRODUCTORY.

In a series of five experimental papers, the author has indicated the mechanism underlying the corrosion of metals. In the first paper[3] it was shown that many metals became seriously corroded when exposed to an atmosphere containing both moisture and also an electrolyte, such as hydrogen chloride or sulfurous acid. Moisture in the absence of the electrolyte, or an electrolyte in the absence of water, had comparatively little effect on the materials. It was suggested that the corrosion might be due to electrochemical action in the film of adherent liquid—a film which, although invisible at the commencement of the process, became visible in the course of the action in those cases where the corrosion-product had a hygroscopic character. Although the existence of the electric currents was not at that time actually proved, the suggestion received support from the special phenomena noticed at the contact between dissimilar metals.

In the second paper,[4] which described the behavior of metallic specimens wholly or partially immersed in water or salt solutions,

[3] U. R. Evans, Trans. Faraday Soc., 19, 201 (1923).
[4] U. R. Evans, J. Inst. Metals, 30, 239 (1923).

the electrochemical character of the phenomenon was actually demonstrated, the current being in many cases tapped. Usually the current was set up by "differential aeration," although in the case of copper other factors were found to be of importance.

It was shown that when two electrodes of the same metal surrounded by the same liquid were joined to a galvanometer, a current was produced if oxygen had access to one electrode, but not to the other; the unaerated electrode functioned as the anode, or corroded pole. This observation served to explain the strange fact that the corrosion of metals by ordinary waters (fresh and salt), although requiring the presence of oxygen, nevertheless tends to become *concentrated at those points to which oxygen has least access,* for instance, in the interior of blow-holes or crevices, or at places where inert bodies, such as glass, porcelain or porous *debris,* rest on the metal. An interpretation of pitting and of localized corrosion, almost the only forms of attack which are of importance to the practical man, was thus found. It was also shown that the membranous walls of zinc hydroxide, which appear on zinc immersed in salt water some way below the water line, were produced by the interaction of the alkali from the cathodic (aerated) area at the water-line with the zinc chloride formed by anodic attack of the unaerated area below; in this case the current could be tapped and measured.

In a third paper,[5] the action of drops of salt water placed on an otherwise dry iron surface was shown to be governed by the same principles. The central portion of each drop, to which oxygen could only slowly diffuse, became anodic, and ferrous chloride was there formed, while the marginal portions where air had access to the metal became cathodic, with the production of alkali. Where the alkali and ferrous chloride came into contact, a white ring of ferrous hydroxide soon appeared, but, as this subsequently became oxidized, a brown membrane of ferric hydroxide was produced over the center of the drop, separating the exterior ring of clear alkaline liquid from the liquid inside, which contained ferrous salts, but no alkali. It was shown that the corrosion of the iron was confined to the area within the membrane. In the external zone, to which oxygen had direct access, the metallic surface suffered no visible change whatever.

[5] U. R. Evans, J. Oil and Color Chemists Assoc., 6, 150; especially p. 154 (1923).

It is natural to attribute the immunity (passivity) of the aerated zone, and also the rise in the potential which is the cause of the current involving the corrosion of the unaerated portions, to the existence of a protective oxide-film or oxygen-film. The protective film—whatever it is—has a certain persistence, for it was shown that even if, after the production of the membrane, the whole surface of the metal was uniformly wetted, the marginal zones of the drops remained immune from rusting, although rusting occurred over the area which was originally dry.[6] But in the case of iron the protective film is invisible.

In the last paper of the series[7] it was shown that where a drop of salt water was placed on copper, the external (cathodic) zones became covered with a film of cuprous oxide, thick enough to give interference colors. Sometimes at the extreme edge, brown cupric oxide was also formed. This fact is instructive because it indicates that the production of tarnish-colors, instead of being a special phase of the corrosion phenomenon, may in this particular case be regarded as the antithesis of corrosion proper. The tarnish-colors appear on the cathodic area, and represent the addition of material; the corrosion occurs at the anodic area, and represents the removal of material. It was found that the accumulation of cuprous chloride, the primary anodic product, in the center of the drop serves to stimulate the process by excluding oxygen from the copper surface beneath it, becoming oxidized in the process to blue basic cupric chloride. Thus both cuprous chloride and ferrous hydroxide, which, according to old theories of corrosion, were held to act as oxygen-carriers or catalysts, really act mainly by functioning as oxygen-excluders.

Considered in connection with the work of Pilling and Bedworth[8] on the direct combination of metals with oxygen at high temperatures, the experiments summarized above indicate why at low temperatures electrochemical corrosion is important, while direct chemical attack produces no serious damage. Direct combination of any metal with oxygen can indeed occur, but since the oxide is formed *in situ,* the oxide film at once begins to interfere with the access of oxygen to the metal below. At high temperatures, where diffusion through the film can take

[6] U. R. Evans, Proc. Cambridge Philos. Soc., 22, 54 (1924).
[7] U. R. Evans, J. Soc. Chem. Ind., 43, 127T; especially p. 129T (1924).
[8] N. B. Pilling and R. E. Bedworth, J. Inst. Metals, 29, 529 (1923).

place comparatively readily, we may obtain a film of visible thickness; at low temperatures, the process may in many cases practically come to a standstill before the thickness needed for the first interference-tint is reached.

But electrochemical corrosion (whether the current is set up through contact between dissimilar metals, or through differential aeration) will not generally lead to the formation of a protective film. Even where an insoluble oxide or hydroxide constitutes the final corrosion-product, it is not formed *in situ,* but is generally the result of precipitation, and, being formed at a sensible distance from the metal, does not interfere unduly with further attack.

Vernon[9] recently suggested that various inconsistencies might be removed by accepting the view that "the rusting of iron was an electrochemical (or electrolytic) phenomenon, in which liquid water played a primary and essential part, whereas the tarnishing of copper was a simple chemical phenomenon brought about by a reaction between gas and metal, water playing a secondary part." He believes that the marked accelerating influence of water upon the tarnishing of copper by hydrogen sulfide is simply a catalytic action. The initial difficulty[10] about accepting this view is that Vernon has himself found that the increase of weight of copper in hydrogen sulfide with the time follows a parabolic curve. He assumes that this is due to the fact that the velocity of attack is controlled by the rate of diffusion of the gas through the film. Such an assumption appears to be inconsistent with the catalytic view since the diffusivity cannot be increased by a catalyst, although it might be increased by an opening agent. The matter is considered more fully in an appendix to this paper, where an attempt is made to see how Vernon's catalytic hypothesis can be reconciled with his experimental facts; but the new experiments described in the present paper suggest that, like ferrous hydroxide and cuprous chloride, which were formerly regarded as catalysts, the water acts not mainly as an oxygen-carrier, but rather as an oxygen-excluder.

The present paper is an attempt to obtain more definite information regarding the mechanism of the attack of hydrogen sulfide

[9] W. H. J. Vernon, Trans. Faraday Soc., **19**, 926, 927 (1923-24).
[10] U. R. Evans, *ibid.*, 907.

on copper, and to study the analogies or distinctions existing between this kind of attack, and a typical case of corrosion, such as the atmospheric rusting of iron. It was considered that it would be helpful first to investigate further the action of sulfur dioxide on iron and zinc, cases of corrosion in which it was known that water played a leading rôle. It has been shown by different investigators that iron,[11] copper[12] and galvanized iron[13] can all be exposed to dried sulfur dioxide for some time without alteration, although they are quickly attacked by that gas in the presence of moisture. The second part of the paper is devoted to the detailed study of the action of hydrogen sulfide on copper. Lastly, an appendix is added, in which the subject of the velocity of tarnishing is discussed, the equations obtained being used to elucidate the experimental results obtained by Vernon[14] in his valuable and extensive work on the subject.

I. THE ACTION OF SULFUR DIOXIDE ON IRON AND ZINC.

On the bottom of a "desiccator-vessel," a layer of concentrated sulfuric acid was placed, and in it a crucible containing 5 grams of potassium metabisulfite; in the upper part of the desiccator was a glass plate covered with filter-paper, on which sheets of iron and zinc, previously rubbed with emery, were laid, being turned down under the glass plate at one end, so as to avoid sliding when the vessel came to be tilted. After allowing the whole to stand overnight, in order to permit the metal to become dry, the vessel was tilted, so as to bring together the acid and the metabisulfite; sulfur dioxide was thus generated. No change was observed in the appearance either of the iron or the zinc after a period of four weeks.

A similar experiment conducted in a vessel containing dilute (normal) sulfuric acid instead of the concentrated acid, quickly caused change on the metals; after the first night (before even the acid and the metabisulfite were brought into contact), the iron was observed to be blackened, no doubt due to the sulfur dioxide produced by the action of water-vapor on the metabisulfite. After mixing the acid and the sulfite, the metals changed rapidly, the

[11] U. R. Evans, *ibid.*, 210.
[12] B. S. Evans, *ibid.*, 919.
[13] P. Siedler, Rauch und Staub, **10**, 46 (1920).
[14] W. H. J. Vernon, Trans. Faraday Soc., **19**, 839 (1924).

iron becoming dark grey with patches of saline substances (ferrous sulfite and sulfate), while the zinc became dull grey with crystalline patches. The effect was most notable on the underside of the specimens, and especially near the end, where the metals had been pressed round the plate, and where there was closest contact between metal and filter paper; we have here another example of specially intense corrosion at the "inaccessible places." To ascertain the effect of using acid of intermediate concentrations, experiments were conducted in broad test-tubes, with loops of iron foil fixed to corks closing the mouths of the tubes; in each loop, a crystal of metabisulfite was placed, while at the bottom of the tube, acid of the chosen concentration was placed. After the tube had stood for one night, to establish hygrometric equilibrium between metal and acid, it was tilted so as to allow the crystal to fall into the liquid, and the effect was observed. It was found that the iron over concentrated acid remained bright and unchanged for ten days, although it became dull grey within a few hours when at the end of that period the tube was opened. The specimen placed in the tube containing 50 per cent acid[15] also remained bright for some time, but five days later it was observed to be becoming slightly dull in places. The specimen placed over 20 per cent acid became dull within a few hours, before even the sulfite crystal was allowed to drop into the acid; after the sulfite had been allowed contact with the acid, darkening occurred rapidly, and in a few hours the surface as a whole was fairly dark, but was covered with numerous circular bright patches. The nature of the bright circles, which are shown in Fig. 1, is discussed below. The specimen over normal acid (4.9 per cent) darkened yet more rapidly, and also became covered with bright circles.

It seemed possible that the corrosion had been helped by the drop of temperature during the night, which would have caused water to condense in liquid form on the metal. But it has been pointed out in a previous paper[16] that there is a possibility of the condensation of water in concavities, even when the air is unsaturated with respect to the level surface of pure water. It appeared

[15] Throughout this paper, 50 per cent acid means acid containing 50 g. of concentrated sulfuric acid diluted with water to a volume of 100 cc. Similarly 20 per cent acid indicates acid with 20 g. in 100 cc., and so on.

[16] U. R. Evans, Trans. Faraday Soc., **19**, 208 (1923).

advisable to carry out an experiment at constant temperature, so as to avoid the type of condensation which is due to periodical variations in temperature. Accordingly, a loop of iron, cleaned with emery, was fixed to a cork and placed in the upper part of a test-tube which contained a small quantity of normal sulfuric acid. After one hour, a crystal of metabisulfite (previously dried by exposure over concentrated sulfuric acid) was placed in the loop; the cork was waxed in, and after five minutes the crystal was allowed to fall into the acid; the whole tube was then totally immersed in a thermostat bath at 25° C.

After two hours, there were signs of the lower part of the iron becoming dull and greyish; after 5 hours, the lower part was dark grey. The darkened portion was fairly sharply divided from a comparatively unchanged area above, but the darkened part extended up into the unchanged part along the emery grooves, an observation which seemed to support the view of preferential condensation in concavities. After 21 hours, the strip as a whole was dark grey, but the surface was covered with numerous tiny bright circles as mentioned above.

The various specimens were taken out of the tubes, and examined under the microscope. The bright circles were found in most cases to have diameters of 0.2 to 0.6 mm., and each bright circle had at its center a small dark nucleus, which seemed to represent a small pit; outside the bright circles, the surface was dark grey. The phenomenon was reminiscent of the bright cathodic areas obtained in previous work on immersed specimens around pits where anodic attack was proceeding, and it was natural to suppose that the central dark spots represented anodic points, and that the circle around them remained bright owing to cathodic protection.

This view was supported by the fact that in certain parts of the specimen microscopic circles of white salt, reminiscent of coral-cups, could be seen around dark spots which seemed to be pits; the circular crusts of salt, some of which are shown in Fig. 3, had a radial structure, suggesting that the salt had "crept," in the well-known manner, out of the pit where it had been formed. The salt composing these circles was white when first observed, but after the specimen had stood a few days in the laboratory air, it was observed to have become yellow through oxidation to the

ferric condition. Apart from these conspicuous crusts, the whole of the dark-grey surface seemed to be covered with a very thin crystalline deposit, but in some places this deposit only became distinctly visible when the surface was rubbed with a fine glass point.

The above experiments were conducted with Griffin's "pure iron foil," but similar results were obtained with steel. Safety razor-blades (first cleaned with alcohol and then dried) when exposed to sulfur dioxide generated from normal sulfuric acid, or from 20 per cent sulfuric acid, became black in a single night; the blade exposed to sulfur dioxide over 50 per cent sulfuric acid was unchanged at the end of one day, but at the end of the week it had become dark in patches. The blade exposed to sulfur dioxide over concentrated sulfuric acid remained bright at the end of a week, and the edge was found still to be sharp.

Mild steel sheet, such as is used at the tin-plate works (provided through the kindness of Prof. C. A. Edwards, of Swansea,) was found to be quickly attacked by moist sulfur dioxide; on the interior of the "loop" a solid cake of salts about 3 mm. in thickness was formed by two days' exposure to sulfur dioxide and air over 20 per cent sulfuric acid; this cake was white in the interior, but had turned brown superficially.

The results are strongly confirmatory of the view that the atmospheric corrosion of iron and zinc in the presence of moisture and sulfur dioxide depends on the same principles as the corrosion of the same metals immersed in water, and emphasize the fact that the presence of water is necessary, if attack is to occur. The matter has some technical importance; some of the most conspicuous cases of corrosion occur where water and sulfur dioxide are produced simultaneously; the author has recently described a case of marked corrosion of iron, bronze and brass articles, which occurred in a room where coal-gas containing sulfur was burned without any provision being made for the escape of the products of combusion.[17]

II. THE ACTION OF HYDROGEN SULFIDE ON COPPER.

Preliminary Experiments. When a sheet of copper,[18] rubbed

[17] U. R. Evans, Chem. and Ind., 43, 506 (1924).

[18] Electrolytic copper foil obtained from the same source as in previous papers was used throughout the research.

clean and dry with coarse emery,[19] is placed in a vessel above the surface of a saturated solution of hydrogen sulfide in water, a sequence of tarnish tints appear, the order of the colors being brown, rose, mauve, blue and steely-grey. Sometimes the order is then repeated, with variations, a matter which is discussed later. If, just before introduction into the gas, part of the surface is wetted and then rendered dry (to all outward appearance) by "dabbing" a piece of filter paper on to the copper, the tints arrive sooner on this area than on the part that had never been wetted, and the colors seem more intense, or at least more uniformly intense, over the area treated.

If, on the other hand, the wetted part of the surface is not wiped dry, but the water is allowed to drain downwards, then, instead of bright tarnish tints, a muddy black or brown appears over the wet part, when exposed to gaseous hydrogen sulfide. The darkening is most intense at the top part of the wetted area, where the water-film, although remaining visible, quickly becomes very thin. The darkening usually follows the emery grooves in this region; these grooves represent places where a thin film of water can remain after the ridges between them have drained themselves dry. Here the blackening occurs extremely quickly; in one experiment, the grooves of the "drained" area were already quite black, at a time when the dry part had shown no change of color at all, and when the area which had been wetted and "dabbed dry" was only just turning to pale brown.

Lower down, where the drainage had produced distinct drops of water, the copper remained unchanged for some time, no doubt owing to the thickness of the liquid covering it. The black or brown sulfide is much looser than the sulfide composing the bright tarnish-films, and is usually thicker, no doubt because it is porous and non-protective. These preliminary observations suggest that two distinct phenomena may be distinguished.

1. Tarnishing proper, that is, *the production of the bright interference colors,*[20] which must be due to a very thin compact

[19] All copper specimens throughout the research were cleaned just before use with Oakey's No. 2 emery paper.

[20] Various investigators have claimed that the colors of thin oxide-films are due to other causes, but recent work by the author on oxide-films on iron and lead has indicated that they are attributable essentially to interference between the waves reflected from the outer and inner surfaces of the film, as has usually been thought to be the case. For normal reflection, a given color will be extinguished when the thickness of the film is equal to an odd number of quarter-wavelengths of light of that color in the material composing the tarnish-film.

film of sulfide in optical contact with the unchanged metal. Presumably the copper sulfide is produced *in situ,* at the place previously occupied by the metallic copper which has undergone the change. It is highly probable, therefore, that we have to deal with a direct attack of hydrogen sulfide and oxygen upon the surface layers of the metallic copper.

2. *The production of brown or black sulfide,* which is clearly less compact and sometimes non-adherent; the dark color is an indication of a somewhat porous character, the light being lost by repeated internal reflection within the passages threading the material, instead of being reflected back to the eye. The transformation of compact metallic copper into this less compact body can scarcely be so simple a process as the production of the continuous film which produces the interference tints. This second phenomenon is better described as *corrosion* than as tarnishing, since it is liable (if followed by rubbing) to lead to the removal of material, whereas tarnishing essentially involves the addition of material. It appeared a matter worth investigation to decide whether this case of corrosion, like so many other cases, is of an electrochemical character.

EFFECT OF AN EXTERNALLY APPLIED E. M. F. ON THE BEHAVIOR OF COPPER IN A SOLUTION OF HYDROGEN SULFIDE.

It seemed clear that the decision just indicated would be reached more easily if information were available regarding the behavior of copper in hydrogen sulfide under the application of an electrical current furnished from an external source. Accordingly an electrolytic cell consisting of two copper electrodes dipping into a solution of hydrogen sulfide was set up, and a small current forced through it. It was found that when a saturated solution of hydrogen sulfide was used, a very small current (1.2 milliamp. for an immersed electrode area of 4 x 3 cm.) was sufficient to prevent blackening of the cathode, and to cause marked blackening of the anode; the anode became much darker on the front facing the cathode than on the back, where the current density was lower. When the current was reduced (to 0.3 milliamp.), the cathode began to blacken at its back, but still remained bright in front, where the current density was higher; when the current

was again increased, the black patch on the back of the cathode slowly began to shrink. Somewhat similar results were obtained with dilute solutions (S/100);[21] the cathode, although not unchanged, remained much lighter than the anode. Apart from the more or less adherent sulfide which appeared on the anode, the liquid around the anode became brown and turbid, and finally a definite brown precipitate appeared.

The experiment just described shows that anodic treatment stimulates, and cathodic treatment reduces, or even prevents, the corrosion of copper by hydrogen sulfide; the facts are thus analogous to other cases of corrosion. It also indicates that the physical character of the copper sulfide formed by anodic action is of a kind unlikely to interfere seriously with further attack upon the underlying metal. Indeed the part which first becomes visible as a precipitate in the solution far away from the metallic surface can clearly have no protective action at all.

EFFECT OF CONTACT WITH DISSIMILAR METALS.

It seemed of interest to ascertain whether the darkening of copper by a hydrogen sulfide solution containing oxygen would be affected by contact with other metals. Accordingly, three strips of copper were prepared; one had a piece of zinc sheet bent over one end and pressed into contact with pliers, another was similarly joined to silver, while the third was not connected to any metal; they were immersed in saturated hydrogen sulfide solution in a shallow porcelain dish for two days and then examined. The independent strip had become brownish-black; the effect of contact with silver was not conspicuous, the copper joined to that metal being scarcely darker than the independent piece. The effect of contact with zinc was, however, very marked; the copper, although slightly brown, was much lighter, especially near the point of contact, than the independent piece. The protective action of zinc was also conspicuous in more dilute solutions; in experiments carried out in S/10 solution, the independent specimen became slaty-black within two days, while that joined to zinc remained almost unchanged near the junction; in S/100 solution the independent copper became a fine brown, while that joined to zinc still remained bright along the line of contact.

[21] The symbol S indicates water saturated with hydrogen sulfide at 21° C.; S/10, S/100, denotes one-tenth, or one-hundredth of this concentration.

PRODUCTION OF AN ELECTRIC CURRENT BY DIFFERENTIAL AERATION.

Clearly, however, under ordinary conditions of service, contact between dissimilar metals will occur comparatively infrequently. Under practical conditions, the accidental setting up of an electric current between different parts of a metallic article occurs most commonly as a result of differential aeration. It appeared necessary to investigate whether a difference in oxygen-concentration was capable of producing a current between various points on a copper surface immersed in hydrogen sulfide.

As usual in the study of copper, the investigation of this matter is rendered difficult by the fact that the bubbling of air over copper produces stirring as well as aeration, and the e. m. f. set up by stirring opposes that set up by aeration. If, however, the difference in oxygen concentration is sufficiently marked, it has been shown[22] that the aeration current in a sodium chloride solution can be demonstrated even with copper electrodes.

To test whether this was possible with a hydrogen sulfide solution also, a divided cell was set up, and both compartments filled with distilled water, which was rendered moderately free from oxygen by boiling. The liquid in the outer compartment was then covered over with paraffin, and the whole was allowed to cool. Hydrogen sulfide was then passed into the liquid on both sides, and finally two copper electrodes were introduced, one into each compartment, and were joined to a microammeter. Air was now bubbled into the inner compartment, and it was seen that a current was produced in the normal direction, the aerated electrode being the positive pole. The current momentarily increased slightly when the bubbling was stopped, no doubt owing to the cessation of stirring, but it then gradually fell off with the time, presumably owing to the exhaustion of oxygen; fresh bubbling caused it to rise again.

If the outer compartment was stirred with a glass rod, while bubbles were passed through the inner one, the current became somewhat stronger, reaching 32 micro-amperes, with electrodes having an immersed area of 12 sq. cm. In this case there was stirring in both compartments, but aeration in only one, and the aeration e. m. f. was therefore not opposed by the contrary

[22] U. R. Evans, J. Soc. Chem. Ind., 43, 127T (1924).

e. m. f. due to stirring. Evidently copper in hydrogen sulfide solution obeys the general law established in the previous researches; the strength of the current obtained from copper by differential aeration is, as usual, much smaller than that obtained from the more easily corrodible metals, such as zinc and iron.

EFFECT OF DROPS OF HYDROGEN SULFIDE SOLUTION ON COPPER.

The practical consequences of differential aeration on the blackening of copper by hydrogen sulfide are best indicated by studying the effect of drops placed on a horizontal copper surface. A number of drops of hydrogen sulfide solution of different concentrations were placed on a copper sheet, freshly rubbed with emery, in a closed vessel containing water (to prevent evaporation). Drops of varying shapes were obtained by dropping the solution on the metal from varying heights. After several hours the specimens were taken out, washed with water to remove loose deposit, dried and examined. The character of the result depended naturally on the shape of the drops, the concentration and other conditions; but in most of the cases four areas could be distinguished (see Fig. 5):

(a) In the dry area, outside the limits of the drop, the metal had become rose-colored, blue or steely, through the gaseous hydrogen sulfide given off; the colors naturally varied with the distance from the drop.

(b) At the edge of the drop, there was a marginal ring of black sulfide.

(c) Within this, there was an intermediate annular zone where the copper, although darker than at the start, was comparatively unchanged.

(d) Lastly, there was a central zone, which was distinctly black, or, in the case of the very dilute solutions, brown.

It is worthy of note that the same four zones could often be distinguished when drops of pure water were dropped on to copper, which was then placed in the upper part of a vessel containing water saturated with hydrogen sulfide. In many cases, a single glance was sufficient to show that zone (c) was far less changed than zone (d); in some instances, however, mere ex-

amination under the microscope was indecisive. In these instances it was found helpful to place a drop of concentrated hydrochloric acid on the areas in question, followed by a stream of water; this treatment converted the cuprous sulfide into white cuprous chloride, which afterwards became yellow-green through oxidation. The result rendered quite evident the fact that zone (c) had contained far less sulfide than zone (d).

The existence of zones (c) and (d) receive an easy interpretation when considered in connection with previous work. As in the case of the drops of salt water on iron, the central area (d), to which oxygen has had but little access, appears to have suffered anodic attack, giving rise to cuprous sulfide, while the zone (c), to which oxygen has had access, has functioned as the cathode.

In the case of the flatter drops, or puddles of liquid of considerable extent and nearly uniform thickness, the division into circular zones cannot usually be made out. In such cases the blackening occurs principally in the grooves left by the emery treatment, and extends from the margin inward along those grooves, as shown in Fig. 6. Now it has been found in previous work[23] that iron covered with a uniform film of water or salt-solution tends to be attacked along the emery-grooves, as illustrated in Fig. 2; the grooves represent the places least accessible to oxygen. The same interpretation suggests itself for the preferential blackening of copper along the grooves. It would seem that while in some drops we are dealing mainly with the effect of the *horizontal* distribution of oxygen (giving rise to circular zones), in others we are dealing mainly with the effect of a *vertical* distribution of oxygen, giving rise to blackening in the depressed places, and comparative immunity upon the ridges between them.

The significance of the black marginal zone (b) has still to be considered. This is a very important matter, since in many cases considerably more blackening was observed round the margin than in the interior. It was noticed that, other things being equal, drops of concentrated solution produced most of the blackening in the marginal portions, the zone (b) being broad and pronounced, while in drops of dilute solution the color-change occurred mainly in the interior. Fig. 5 shows the effect of a drop

[23] U. R. Evans, Proc. Cambridge Philos. Soc., 22, 54 (1924).

of saturated hydrogen sulfide on the right, and that of a drop of S/100 solution on the left.

At first sight the blackening at the margin would seem to be the result of direct chemical action occurring along the line where copper, hydrogen sulfide and oxygen had come together. The aspect of the deposit, however, does not support the view that it is a direct product in the same sense as the compact copper sulfide which causes the colors on the dry area (a). Now previous experiments on the corrosion of copper in other liquids (*e. g.,* dilute sulfuric acid) have indicated that the strip along the water-line itself is frequently an anodic area. In the case of a drop resting on copper, owing to negative adsorption[24] at the water-air interface, there will actually be a considerably lower copper-ion concentration at the margin, that is, in zone (b), than just inside it, that is, in zone (c). Since oxygen is only slowly used up, the oxygen concentration will not differ much in these two zones, and consequently the direction of the e. m. f. will be determined by the concentration of copper ions; the zone (c) will be cathodic and the marginal zone (b) will be anodic and will become blackened with sulfide.

It seems, however, that much of the sulfide seen at the margin of the drop is not actually at the copper-liquid interface, but is really at the liquid-air surface. It was noticed that at the extreme edge of some of the drops of hydrogen sulfide, a thin membrane seemed to be growing upwards over the surface of the liquid. A much more conspicuous membrane appeared upon the sides of drops of pure water placed on a copper sheet in an atmosphere of hydrogen sulfide, and in such cases the membrane soon came to extend over the greater part of the top. The membrane, which had a bright silvery appearance, was found to be dissolved slowly by hydrochloric acid without turning white; it was evidently *cupric* sulfide, in contradistinction to the black deposit formed on the anodic parts of the copper itself, which was *cuprous* sulfide. It seems probable that the membranous body was a precipitation product; possibly the initially formed cuprous sulfide was oxidized locally to soluble cupric sulfate, which diffusing outwards to the

[24] W. H. Whatmough, Zeitschrift für physikalische Chemie, **39**, 129 (1902), examined the surface tension of numerous salts, and found that in every case it is higher than that of pure water. This means that salts must be negatively adsorbed at a water-air interface, although at a water-solid interface, as is well known, either positive or negative adsorption may occur.

places where hydrogen sulfide was in excess, yielded a precipitate of cupric sulfide; it is a fact well known to analysts that precipitated copper sulfide tends to adhere as a membrane to the air-liquid interface.

WATER-LINE PHENOMENA.

Similar zones were observed when a strip of copper was allowed to stand in a vertical position half-immersed in a solution of hydrogen sulfide, the part above the water-line being wetted with a film of liquid. The appearance of a specimen treated in this way for two days, and then taken out, rinsed and gently rubbed, is shown in Fig. 4. The part above the water-line was found to be covered with a loose black crust of sulfide when the specimen was removed, but this peeled off on gentle abrasion, leaving bright metallic copper below. At the water-line, there remained a dark line of much more adherent black sulfide. Below this came a line of bare copper, unchanged except for a slight brown tarnish. At a lower level, the copper was again covered with a fairly adherent sooty deposit of sulfide, which possessed a curious whitish sheen, causing it to appear comparatively light in the photograph; this extended downwards, following the emery scratches, to the bottom of the specimen. In some of the specimens of copper half-immersed vertically in a solution of hydrogen sulfide, the existence of a membranous rim of sulfide extending outwards from the metal along the surface of the liquid was clearly shown.

The explanation of the zones described above would appear to be analogous to that of the zones produced within the drops of hydrogen sulfide solution placed on a horizontal surface.

EXPOSURE OF DRY COPPER IN TUBES OVER HYDROGEN SULFIDE SOLUTION.

Having examined the effect of the simultaneous presence of liquid water and hydrogen sulfide on copper, it is now possible to return to the behavior of (initially) dry copper exposed to an atmosphere containing both moisture and hydrogen sulfide in varying amounts. The following nine experiments were conducted simultaneously in glass tubes of diameter 2.5 cm. and length 18 cm. placed on a bench in the laboratory. The temperature of the room rose gradually from 13.2° C. at the commencement of the observations to 20.5° C. at the end. Each of the nine tubes

contained a strip of copper 5 cm. x 1.5 cm., suspended from the cork, and in the lower part was liquid containing a known concentration of hydrogen sulfide (S/2, S/20 or S/200). In three of the tubes, the copper strips had been wetted with distilled water and "dried" between filter-paper immediately before use; in the remainder the metal had received no wetting at all after being rubbed with emery.

It was found that the coppers exposed over S/2 solution reached the early stages of the color-sequence much more quickly than those over S/200 solution. Thus in 36 minutes, the specimen placed over S/2 hydrogen sulfide had passed through the brown, and rose stages, and was already mauve (and even bluish along certain lines following the grooves), while that placed over S/200 hydrogen sulfide was still unchanged over the greater part of the surface, although the lowest 1.5 cm. had turned brown, and even rose had appeared along the bottom edge. On each of the specimens over S/2 solution, the upper part was, as a whole, practically of the same hue as the lower part, the distribution of tints tending rather to follow the emery-grooves. On the other hand, on the specimens over S/200 solution, owing to the correspondingly small amount of hydrogen sulfide in the tube, the series of tints commenced at the bottom and the sides—the places where gaseous diffusion would be most active—and gradually extended upward and inward. For this reason, no doubt, one obtained after 7.5 hours simultaneously upon a single strip, the whole series of tints up to the blue of the third order. Later other tints arrived, and it was possible to tabulate the complete sequence of colors[25]:

Brown.....	First Order Tints
Rose.....	
Mauve.....	
Blue.....	
Steely-Gray	
Yellow.....	Second Order Tints
Brown.....	
Rose.....	
Blue.....	
Green.....	
Brown.....	Third Order Tints
Rose.....	
Blue.....	
Green.....	
Dirty Rose.....	Fourth Order Tints
Dirty Green....	
Relapse into gray follows.	

[25] The colors are roughly complementary to that of the wavelengths extinguished. Thus brown is produced by the extinction of the blue rays; rose occurs when the film is thick enough to extinguish the longer green rays, and so on. The first order tints correspond to a difference of 0.5 wavelength between the paths of the rays reflected from the two surfaces; the second-order tints to a difference of 1.5 wavelengths, while the third and fourth order represent differences of 2.5 and 3.5 wavelengths, respectively.

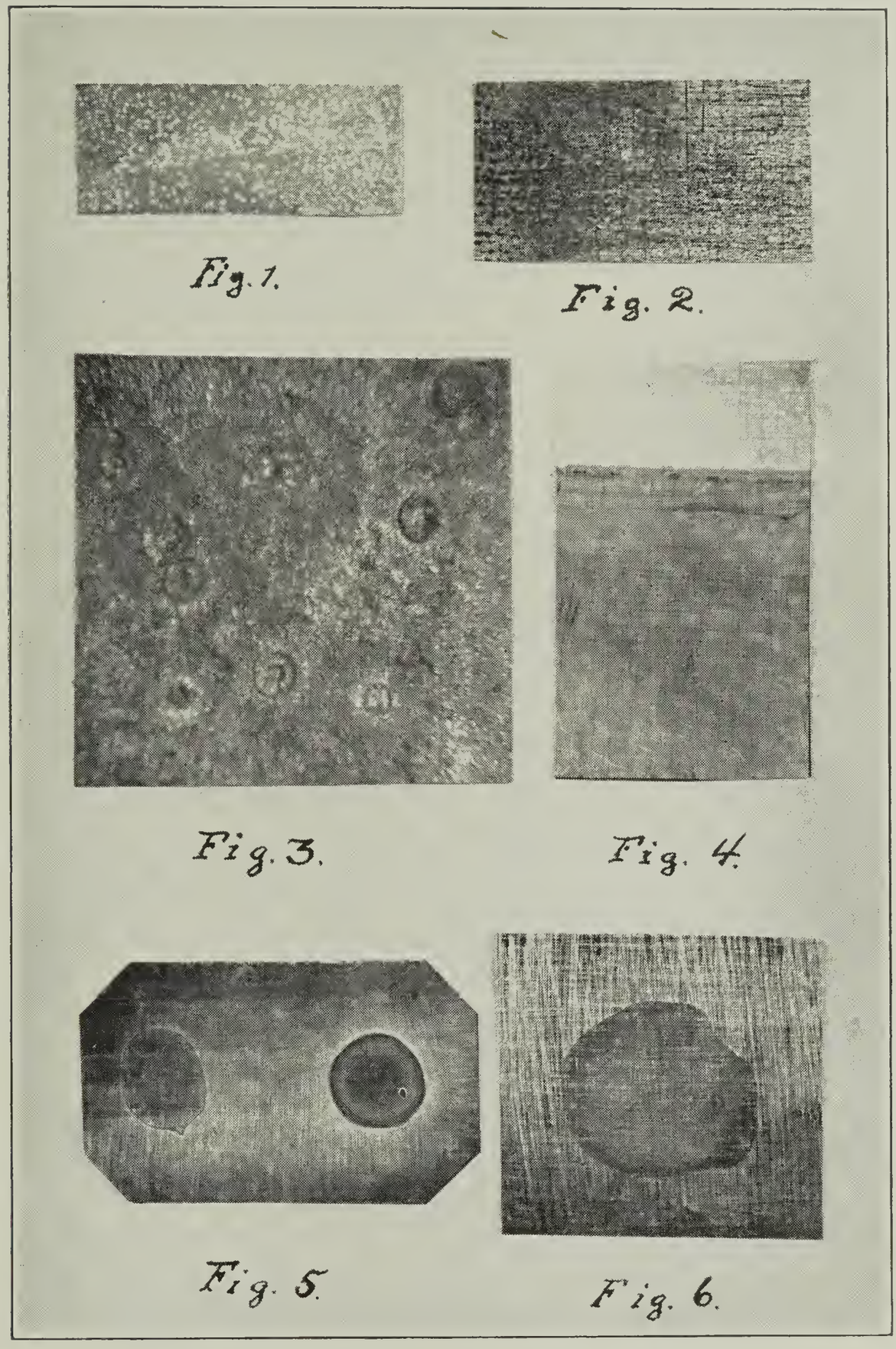


FIG. 1. Iron exposed to moist sulfur dioxide (x 1.2).

FIG. 2. Iron allowed to rest beneath a thin layer of water (x 0.9).

FIG. 3. Iron exposed to moist sulfur dioxide, another area (x 15).

FIG. 4. Copper half immersed in hydrogen sulfide solution and afterwards gently rubbed. (Natural size.)

FIG 5. Effect of drops of hydrogen sulfide solution on copper (S/100 on left, S on right) (x 0.9).

FIG. 6. Effect of shallow patch of hydrogen sulfide solution on copper (x 1.2).

The tints were much brighter over the S/200 solution than over the S/2 solution; over the stronger solution, they were somewhat dull from the start, and after the end of the first order, it was difficult to make out the appearance of the various colors with certainty, the specimen remaining a dirty grey throughout the rest of the run. One of the most interesting differences between the behavior of the two series was that over the S/2 solution the specimen which had been "wetted and dried" became colored more quickly than the specimen which had not been wetted, while over the S/200 solution, the reverse was the case. This phenomenon, which was verified by separate experiments, indicate that the part played by water may be more complicated than at first sight would appear to be the case.

Copper strips were also exposed over S/20 hydrogen sulfide, and these showed an intermediate behavior. The appearance of the various tints was at first practically as rapid as over the S/2 solution, and the specimen which had previously been wetted assumed the various colors more quickly than the other. But the colors were brighter than over the S/2 solution, and, although in the early stages the colors tended to follow the lines of the grooves, just as on the strip over the S/2 solution, in the later stages they were arranged in zones parallel to the bottom and edges of the strips, as on the strip over the S/200 solution.

Three experiments were also conducted in tubes over liquid containing 25 per cent sulfuric acid, besides hydrogen sulfide (S/2, S/20 and S/200). The sulfuric acid was intended to reduce the tension of aqueous vapor. The copper strips, however, did not show any important difference in behavior to those placed above the solutions free from sulfuric acid. The reason may be that no time was allowed for the copper to come to hygrometric equilibrium with the acid before tarnishing commenced.

The observations just described were conducted in the ordinary laboratory, without serious complications due to the second form of attack, because the temperature was rising steadily, and thus no condensation of liquid water on the metal occurred. After the observations, the tubes stood in the laboratory for two nights, and it was then found that on the lower part of the strips over the S/2 solution the sulfide layer was peeling off in black flaps, apparently due to the local condensation of moisture. In the tubes

which originally contained S/200 solution the strips showed no peeling, and the colors were undimmed, probably because the hydrogen sulfide was already exhausted at the time when water began to condense.

The effect of the condensation of water is shown more clearly in the following experiment. Tubes containing copper strips over S, S/10, S/100 and S/1000 hydrogen sulfide were wholly immersed in a thermostat at 25° C. for four hours, and were then removed and allowed to stand in the laboratory. After 24 hours these tubes were again examined. In every case visible moisture had condensed on the lower part of the strip and had caused marked changes; in the S/100 and S/1000 tubes, the copper, although showing interference tints elsewhere, was black or brown where wetted. In the S/10 tube, the deposit was of a dull black adherent character over the upper part, but where visible moisture had condensed there was a silvery flap which could be rubbed off with the finger, revealing below it a ring of bare copper surrounding a circular patch of sooty black sulfide. The whole phenomenon was analogous to that produced by placing drops of water on copper in the presence of hydrogen sulfide, and indicated that the function of the condensed water was probably to set up electrochemical action connected with differential-aeration currents.

To test this possibility, two portions of a strip which had been exposed to hydrogen sulfide for a sufficient time to give colors of the third and fourth orders were cut off, and a drop of water was placed on each. One portion was placed in a closed vessel over saturated hydrogen sulfide solution; the other was placed over pure water. In the first case, loosening of the dark layer occurred within 40 minutes, and on rubbing away the flap, the usual annular zones characteristic of electrochemical action appeared below. In the absence of hydrogen sulfide, water produced no loosening in the time allowed. Other experiments showed that a drop of water free from hydrogen sulfide placed on copper covered with a sulfide layer of thickness corresponding to second-order tints is able, in the course of a night, to cause a certain darkening of the area covered.

It was clearly better to work under conditions of constant temperature, so as to avoid accidental condensation of moisture. Two series of experiments were conducted in the following man-

ner. Small quantities (usually 5 mg.) of iron sulfide were weighed out and each placed into the bottom of a large test-tube; a small tube was placed in each large tube, and into this was delivered 2 cc. of sulfuric acid of known concentration. A cork to which a strip of copper was fixed was then introduced into each large tube, and waxed in, and the whole tube was immersed in a thermostat bath at 25.5° C. After standing for one night, to bring the metal and liquid into hygrometric equilibrium, the tubes were tilted four times, so as to cause the acid to flow out into contact with the iron sulfide, and thus generate hydrogen sulfide. The tubes were then replaced and the appearance of the various colors was watched for. Under these circumstances, it was possible to obtain the series of colors mentioned above, and to reach the higher orders, without the appearance of the brownish porous sulfide, or of the peeling silvery flakes.

A third series of experiments was carried out in which (in the place of iron sulfide) potassium sulfide was employed, a substance which is capable of evolving hydrogen sulfide even from concentrated sulfuric acid. These experiments indicated that in the presence of the concentrated acid, the tarnishing proceeded much more slowly than in the case of dilute acid, thus confirming previous observations that small amounts of water vapor stimulate the tarnishing. Potassium sulfide, however, was an unsatisfactory material to work with, since it gave off hydrogen sulfide in the presence of moisture alone and consequently some of the strips were slightly tarnished at the bottom even before the acid was allowed direct access to the sulfide.

THE ROLE OF WATER IN STIMULATING THE ATTACK OF COPPER BY HYDROGEN SULFIDE.

The effect of the condensation of liquid water, even in a quantity so small as to escape ordinary observation, is scarcely in doubt. It allows the formation of copper sulfide to take place in a manner which does not lead to the formation of a continuous protective film. It is well known that the co-operation of oxygen is needed for the attack of hydrogen sulfide upon copper. It is also well known that the immediate presence of oxygen "on the spot" is prejudicial to any corrosive action, owing to the protective or ennobling effect of an oxide film.

The electrochemical mechanism allows the oxygen to act, in effect, "from a distance." Hydrogen sulfide is about 90 times as soluble in water as oxygen; consequently hydrogen sulfide is able to reach readily parts of the surface which are comparatively inaccessible to oxygen. For instance, in a drop of water placed on smooth copper, the hydrogen sulfide will reach the central portion, while oxygen will only reach the margin; similarly, in a thin layer of water spread over an emery-furrowed surface of copper, hydrogen sulfide will penetrate down into the troughs, while oxygen will only attain to the ridges.

In each case the oxygen renders the parts to which it penetrates protected and cathodic, stimulating the anodic attack upon the copper at the other parts, with the result that we get blackened areas in the center of the drops, or along the lines of the emery-grooves. In other cases the electric current may be set up in other ways. However it is produced, it is probable that since the anodically produced copper sulfide is non-protective, the attack will generally proceed at a moderate velocity, provided that the water film is not so thick as to restrict seriously the access of hydrogen sulfide also to the metal.

The question arises as to whether something of the same kind may not be occurring where the film of moisture is so uniform in thickness that electric currents cannot be generated by differential aeration or by capillary action. If the copper lacks uniformity, chemical or physical, electric currents can, of course, be set up owing to the differences in the potential at different points. But let us consider a case where, either owing to the extreme uniformity of the copper or owing to the extreme thinness of the film of liquid, electric currents, in the ordinary sense, are precluded altogether. In such a case there can be no separate anodic and cathodic areas. Nevertheless the presence of the water film would still promote the reaction; for if it reduces the amount of the oxygen reaching the metal to the amount needed for the reaction,

$$2Cu + H_2S + O = Cu_2S + H_2O$$

it may, to a considerable extent, prevent the formation of an obstructive oxide film, while allowing the production of the relatively permeable sulfide film.

Under such circumstances, we may expect to obtain a continuous film of sulfide, yielding interference colors, as in the absence of moisture, but more speedily. This is actually observed in practice when a very thin (invisible) film of water is present on copper, provided that hydrogen sulfide is present in the atmosphere in large amounts. The fact that a very thin (invisible) film of water actually retards tarnishing when the concentration of hydrogen sulfide in the air is very low, is itself in accord with the view that some sort of "screening" action is at work.

While further research on the subject is certainly desirable, it is believed that the view that water acts as an "oxygen-excluder" better explains the facts as they are known today, than Vernon's suggestion that water acts simply as an ordinary catalyst. As explained in the appendix which follows, the facts are not necessarily inconsistent with the view that water may, in the early stages, stimulate the action catalytically. But it is difficult to think that any catalytic influence of water can stimulate the reaction under conditions where the velocity is already obeying the parabolic law. On the other hand, Vernon's statement that the attack of hydrogen sulfide upon copper is mainly a direct chemical action appears to be perfectly correct if taken to apply to conditions of low humidity. The relative importance of direct chemical action and indirect electrochemical action depends largely on the relative amounts of hydrogen sulfide and water present. In the presence of much moisture, electrochemical action becomes most important. Probably it is in general correct to say that electrochemical action causes most material damage, but that direct chemical attack causes an equally striking change in the appearance of the metal.

APPENDIX.

THE VELOCITY OF TARNISHING OR ATMOSPHERIC CORROSION, WITH SPECIAL REFERENCE TO THE INTERPRETATION OF VERNON'S WORK.[26]

If a tarnish film attains a thickness y in time t, and if the concentrations of the tarnishing agent on the air surface of the film be C_0, and that on the metal surface be C_1, we can write from the ordinary law of diffusion

[26] W. H. J. Vernon, Trans. Faraday Soc., 19, 839 (1923).

$$\frac{dy}{dt} = \frac{k_0}{y} (C_0 - C_1)$$

where k_0 is a physical constant depending on the permeability of the tarnish film to the tarnishing agent. Again from the ordinary chemical law of reaction, assuming that one molecule of the tarnishing agent takes part in the reaction, we can write

$$\frac{dy}{dt} = k_1 C_1$$

where k_1 is the chemical reaction constant. Eliminating C_1 we get the general equation

$$\frac{dy}{dt} = \frac{k_0 k_1 C_0}{yk_1 + k_0} \qquad (1)$$

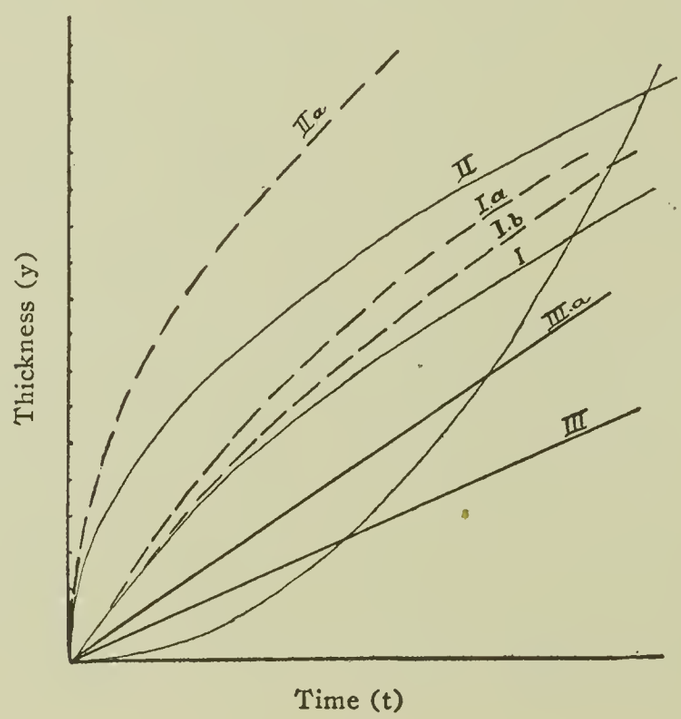


FIG. 7.

Such an equation is represented by a curve of the Type I, Fig. 7. Since both k_0 and k_1 occur in the equation, the velocity will be augmented either by a *catalyst,* which will increase k_1, or by an *opening agent,* which will increase k_0. Obviously a catalyst will affect mainly the initial part of the curve, increasing the initial velocity, and producing a new curve (*e. g.,* Ia), which will, however, be roughly parallel to I in its later stages. On the other

hand, an opening agent will not affect the initial gradient, but will cause a new curve, such as Ib, which diverges from I more and more as the film thickens.

It is instructive to note two limiting cases:

1. When k_0 is very small compared to yk_1, that is, when the physical diffusion is so sluggish as to be the only factor controlling the reaction, equation (1) becomes

$$\frac{dy}{dt} = \frac{k_0 C_0}{y} \tag{2}$$

the ordinary equation of a parabola (Curve II). Vernon has found that his results for the tarnishing of copper in London air closely follow such an equation. Since k_1 does not occur in this equation, clearly the velocity cannot be affected by a catalyst, but can be accelerated by an opening agent, which will alter the curve to another parabola having a different constant (Curve IIa).

2. When yk_1 is very small compared to k_0, that is when the layer is so porous as not to restrict the change, which is determined solely by the chemical rate of reaction, equation (1) becomes

$$\frac{dy}{dt} = k_1 C_0 \tag{3}$$

This is the equation of a straight line (Curve III). Vernon has obtained such a relation in the tarnishing of zinc in an unsaturated atmosphere. Since the equation does not contain k_0 the velocity will clearly not be affected by an opening agent, but will be increased by a catalyst, which will produce another straight line with a steeper gradient (Curve IIIa).

Considering then the question as to whether water can act as a *catalyst* in the tarnishing of copper, it would seem that when once an accurately parabolic form of curve has been reached, the presence of a catalyst can increase the velocity no further. Vernon has published experimental data to show that the curve of the tarnishing of copper in an unsaturated atmosphere follows an accurately parabolic course, and yet states that water acts as a catalyst—two connections, which, as has been already pointed out,

are not easy to reconcile. It may, however, be possible to reconcile Vernon's experimental results with his catalytic hypothesis by considering the following points:

1. Vernon's demonstration that water stimulates tarnishing depends on experiments lasting only a few hours, while the first point on his "parabolic" curve was obtained after 11 days from the start of the experiment; clearly there may have been a considerable initial departure from the parabolic curve, which would not be recognized by points obtained 11 days later. It will be noticed that if k_0 and k_1 are of the same order of magnitude, the general equation (1) will always assume a parabolic form for large values of y; the fact that Vernon's long-period curve showed a parabolic form need therefore occasion no surprise.

2. The catalytic view does not preclude the fact that the *catalyzed* reaction may have a parabolic course practically from the origin. Possibly in the absence of water vapor, the change may follow the general equation (1); in the presence of the catalyst, k_1 becomes so large that the equation reduces to the parabolic form (2). Vernon has apparently not yet studied the course of the reaction in the absence of water.

Therefore, while the author believes that the catalytic view taken alone affords, in any case, a less satisfactory interpretation of the facts than the views expressed in the body of this paper, it it fair to say that the argument advanced by him against it on a previous occasion[27] would cease to be conclusive, if Mr. Vernon would accept the possibility of a small departure from the parabolic form. In order to study experimentally the initial part of the tarnishing curve, the gravimetric method is useless, and the method of interference colors is rendered difficult owing to the color of metallic copper. Preliminary experiments on this point, however, have indicated that it would not be impossible to obtain fairly accurate thickness-time curves with four (or perhaps five) points on each curve, by taking advantage of the fact that the ratio of the thickness of the films having the rose-tints of the first, second, third and fourth orders is 1 : 3 : 5 : 7.[28]

[27] U. R. Evans, *ibid.*, p. 907.

[28] *Not* 1: 2: 3: 4, as assumed by G. Tammann and W. Koster, Z. anorg. Chem., **123**, 196 (1922).

DISCUSSION.

R. J. McKay[29]: Mr. Evans has been one of the principal exponents of the electrochemical theory, and he says here that the relative importance of direct chemical action and indirect electrochemical action depends largely on the relative amounts of hydrogen sulfide and water present. He thus definitely assumes that there is an action here which it not electrochemical. It seems to me that this apparent digression may depend on the use of terms, and certainly in the Electrochemical Society we should be sure to use such terms correctly. Dr. Desch speaks of all corrosion, or at least the fundamental action of corrosion, as *electrolytic*. Here we speak of it as *electrochemical*. These terms are somewhat different, and we should be clear on the point. Also the question of tarnishing and corrosion. It is not clear whether Mr. Evans means to say that tarnishing is corrosion or not.

There are considerable data given by Mr. Evans for corrosion in atmospheres of sulfur dioxide. These "atmospheres" are not sufficiently described as to concentration. The Bureau of Mines has, in some very thorough work, described methods of controlling gaseous atmospheres, including particularly the gas sulfur dioxide, and it seems to me in studying corrosion we should be as exact as in other scientific studies and define conditions as closely as is practically possible.

Another important point of Mr. Evans' paper is the question of differential aeration. At the top of page 259 there is quite a thorough discussion of this question. In 1916 Mr. James Aston presented a paper before this Society[30] showing the production of definite currents of electricity on iron electrodes by aerating one electrode and not aerating the other. He measured those currents and gave valuable quantitative data. It seems to me this question has not received the interest that it deserves in corrosion study. I delivered a paper before you[31] in 1922 on cells due to differences in copper concentrations in the corrosion of non-ferrous alloys by sulfuric acid, and in the course of that paper showed that such cells, in common with cells due to differential aeration, are con-

[29] Supt. of Technical Service, International Nickel Co., New York City.
[30] Trans. Am. Electrochem. Soc., **29**, 449 (1916).
[31] Trans. Am. Electrochem. Soc., **41**, 201 (1922).

centration cells and their action is quite general. In fact, wherever there are two appreciably different concentrations of the corroding agent you will find an e. m. f. set up, and in a great many cases this is the controlling factor—certainly in the localization of the corrosion and probably in the amount.

T. B. HINE[32]: This question of differential aeration, it seems to me, is one of considerable practical importance in connection with a number of forms of corrosion. The thing that I have particularly in mind is the so-called powdering of zinc surfaces, where zinc has been put on iron surfaces for protection, either by hot galvanizing or by electrodeposition. At times we have a powdering effect on the zinc surface, and at other times we have an apparently perfectly continuous and homogeneous surface on the zinc. Whenever this powdering occurs corrosion is generally quite rapid. The conditions under which I have observed on several occasions this powdering of zinc were conditions where there was not a free air movement, but where by alternating cooling and warming up deposition of water could apparently occur in droplets. In that case you would have this type of differential aeration around the droplet that might cause a rather intense local corrosion, and it seems to me that this may be the cause of this powdering effect on zinc.

J. A. PARSONS[33]: We have been making a special type of aluminum bronze, used quite extensively for riser pipes in 10 per cent sulfuric acid for pickling. These pipes are installed in such a manner that one portion is exposed to the atmosphere while the other part remains submerged. Differential aeration, no doubt, plays an important part in instances of this kind. Since some installations were successful while others were not, it occurred to us that perhaps certain non-metallic inclusions or segregations of constituent metals were functioning as cathodes, and not the entire aerated portion. By making use of the differential aeration test cell recommended by Mr. Evans in a previous article, this supposition was actually verified and we concluded that actual homogeneity of the alloy would contribute largely toward the elimination of such types of differential aeration. The study of this type

[32] Research Chemist, Western Electric Co., Chicago, Ill.
[33] Experimental Engr., Duriron Co., Dayton, Ohio.

of electrolytic corrosion will aid materially in improving corrosion resistant alloys.

B. D. SAKLATWALLA[34]: Has Mr. McKay any clear distinction in his mind between the direct chemical action and the indirect electrochemical action, where you can definitely separate the two and come to some terminology between the electrolytic action and the electrochemical action?

R. J. MCKAY: The best physical chemists today assume that all chemical action is, in a sense, electrochemical. The fundamental units of electricity are the fundamental units of chemistry, and any chemical reaction may thus be called electrochemical. The term electrolytic to me means a chemical action in which there is produced measurable electric currents. The difference disappears at the limiting values, as does the difference between physics and chemistry for instance, but there is a definite field for the two terms. Electrochemical is a broader term and the two are therefore not exactly synonymous and should not be so used.

B. D. SAKLATWALLA: Do I understand that it is a matter of difference in degree of the size of the members forming the electrolytic cell? If it is microscopic it is electrolytic, and if it is ultra-microscopic it is chemical.

R. J. MCKAY: That would be my general idea. For instance, consider the corrosion of a steel ball by natural water. We will all agree that when that corrosion starts the most important phenomena are electrolytic in character. That is, anodic and cathodic areas are visible on the ball, and by that means we determine that the two parts of the corrosion reaction are taking place at different places on the ball. Now imagine that the ball becomes smaller and smaller until only one molecule of iron is left; that one is also corroded but no measurable current could pass. The action may be called electrochemical, but I would hardly say it is electrolytic. If the ball is corroded by strong acid, no distinctly anodic or cathodic areas develop at all.

B. D. SAKLATWALLA: Do you then assume that you can have electrolytic action between the same chemical molecules or between two identical chemical molecules?

[34] Vanadium Corp. of America, Bridgeville, Pa.

R. J. McKay: Not between two identical chemical molecules, but it seems to me that the action is fundamentally the same when it takes place with two molecules which are perfectly adjacent. You may then have the reaction divided into two parts, and two identical molecules both take part in it, and charges pass from one molecule to another of the same identical composition, but if there is only one molecule of a kind you may have the same reaction taking place. Fundamentally the action is the same. The only difference is that in one case there are two molecules taking part and in the other only one.

B. D. Saklatwalla: Then, as I understand you, it amounts to this: You can have chemical action without electrolytic action, but you may have electrolytic action as an intensifier of chemical action.

R. J. McKay: Yes, I would agree to that.

W. H. J. Vernon[35] (*Communicated*): I have read the present contribution with the greatest interest, and believe that it serves an eminently useful purpose. Hitherto attention has been mainly focused on the mechanism of corrosion in electrolytes, in the elucidation of which Mr. Evans has taken so important and valuable a part. The special case of tarnishing in unsaturated atmospheres at ordinary temperatures has indeed received the attention of Mr. Evans in a previous communication[36], but on that occasion it was suggested that the mechanism was essentially electrochemical, comparable with that which obtained on immersion in an electrolyte. In the light of his further experimental work, the author has modified his views in this direction, and I am grateful to him for the frankness with which these views are stated and discussed in the present paper. I am interested, moreover, to note that the reasons which have led him to adopt the "chemical" interpretation of tarnishing are substantially the same as those which weighed with myself and prevented my accepting the "electrochemical" explanation.

So far as the purely tarnishing side is concerned, my own experiments have been largely held up, owing to pressure of work in other directions. This, however, only serves to increase my

[35] British Non-Ferrous Metals Research Assoc., London, England.
[36] Trans. Far. Soc., **19**, 201 (1923).

interest in the further experimental evidence which Mr. Evans now adduces, especially seeing that this throws most useful light on certain doubtful points in my admittedly incomplete work. Thus, the communication to which Mr. Evans so generously refers ended in a note of doubt.[37] Employing ordinary (polluted) air, I had found that by greatly increasing the humidity (resulting presumably in the precipitation of moisture on the metal surface) the tarnishing of copper was largely inhibited. Experiments with hydrogen sulfide, however, gave the reverse result, and I concluded that "the action of hydrogen sulfide does not provide an analogue of the tarnishing effects actually observed in the atmospheres under observation."

Mr. Evans now shows that this is all a question of concentration, and that by employing sufficiently low concentrations of hydrogen sulfide one obtains a perfectly satisfactory analogy. The phenomenon is certainly a curious one, and an explanation is desirable, although apparently not immediately forthcoming. Possibly for very low concentrations of sulfide in the atmosphere, the concentration of oxygen in the water-film is sufficient to oxidize invading molecules of H_2S before they can reach the metal. Alternatively, the presence of water may cause a thickening of the protective film of oxide or hydroxide, which may thus offer greater resistance to attack than the relatively unoxidized metal. The opinion of the author on this point would, however, be acceptable.

As regards the mechanism which would be attributed to the "tarnishing" process, it will be evident that Mr. Evans and myself are now in agreement on the major issue; I would indeed suggest that such differences as may still appear from a first reading of the paper are more apparent than real. Thus, referring to the accelerating influence of water, I am quite ready to concede that its function here is that of an "opening agent," and would like moreover to congratulate Mr. Evans on the neatness of the arguments he has advanced. But the fact remains that a reaction has been accelerated by the presence of a substance which itself does not appear in the end product, and according to the usual definition this is surely catalysis, and the term "opening agent" merely a cumbersome substitute for "catalyst."

[37] *Ibid.*, **19**, 900 (1923).

It is true that the process involved in the present instance is essentially a physical one, but to reject it as catalysis on that account would certainly be contrary to accepted usage. At the same time it would be idle to pretend that I do not appreciate the distinction which Mr. Evans has in view, and indeed I consider that the distinction has been most usefully emphasized by him. In this connection it is of interest to recall the terms proposed by Rosenoff[38] to indicate the two main groups into which catalysts may be divided, namely, "direct" and "indirect" catalysts respectively.

These two terms appear to be capable of most useful application in the present instance. Thus, instead of the alternatives presented by Mr. Evans as to whether water is to be regarded as a catalyst or an "opening agent," we should have to consider whether it functions as a direct or as an indirect catalyst. In order to settle this question it would certainly be of great interest, as Mr. Evans points out, to ascertain the precise form of the early part of the time-thickness curve for various degrees of desiccation. In the meantime, however, it does seem most reasonable to suppose that the results would confirm the view that the function of water is actually that of an indirect catalyst.

There remains one further point I desire to raise and this is suggested at once by the title of the paper. Apparently Mr. Evans is not content with excluding tarnishing from the electrochemical fold, but he must needs place it outside the pale of corrosion. While attaching the greatest value to Mr. Evans' work, in connection not only with tarnishing but with corrosion in general, I must confess that he does not carry me with him in the view that tarnishing and corrosion are two essentially distinct phenomena. I have always understood that corrosion was the attack upon a metal by chemical processes, or to put it more precisely, the *oxidation*[39] of a metal, according to which definition tarnishing assuredly is corrosion, albeit in early stages. I agree emphatically, however, that it is a special phase of the more general problem, and one which calls for quite special attention.

As I understand Mr. Evans in the text tarnishing, that is, a direct chemical attack, is not corrosion because no material is

[38] J. Amer. Chem. Soc., 35, 173 (1913).
[39] *Vid.*, Bengough and Stewart, J. Inst. Metals, 28, 38 (1922).

removed. But surely this is only a matter of degree. Consider, for example, the tarnishing of copper by hydrogen sulfide. It is evident that the attack upon the metal continues after the sequence of colors, which the author so ably analyzes on page 264, has been passed. I have found that after a time (the whole system being enclosed[40] over P_2O_5) the scale exfoliates, and the state of affairs then corresponds exactly with that which the author describes on page 257 as corrosion, an accumulation of loose, friable material resulting; indeed, no "rubbing" is required to effect its removal.

On the other hand, there are cases of acknowledged electrochemical corrosion where the products happen to stick to the metal surface in the early stages. Yet, again, cases may be cited, for example Zn and Al, where on exposure to the atmosphere the metal suffers no particular color change, and hence can not be said to "tarnish," and yet undoubtedly becomes covered with a scale which adheres very firmly. Moreover, in this instance there is no reason to suppose that the scale is produced by other than a chemical process, as with tarnishing, except that its physical properties are such that perfect continuity is not insured, and hence interference colors are not developed. See Pilling and Bedworth's work at high temperatures, where they show that a quadratic parabola about the time axis corresponds with a perfectly continuous scale, and a straight line, such as I have obtained independently for zinc at ordinary temperatures, corresponds with a scale of discontinuous or "cellular" character.

The one feature common to all these examples is that the corrosion product adheres to the metal from which it is derived, resulting in a gain in weight of the specimen. Clearly, a special term is desirable to indicate this state of affairs, but it will be equally clear that "tarnishing" does not meet the need. Fortunately, a suitable expression is forthcoming in the word surrosion (French, *sur,* on), proposed by Dr. Newton Friend. In the course of my own work I have found this word exceedingly useful, and the present paper only serves to convince me of its utility. Thus, surrosion is that special case of corrosion, whether "chemical" or "electrochemical," or whether resulting in color change or leaving the metal apparently unaltered, where the product adheres to the metal, and so gives an addition rather than a removal of material.

[40] As described in J. Inst. Metals, 30, 287 (1923).

Ulick R. Evans (*Communicated*): I am in agreement with much of what Mr. McKay has said. I am acquainted with Mr. Aston's important work on differential aeration, and have alluded to it in other papers. Mr. Aston was, I believe, the first to call attention to the currents set up by differences in oxygen-concentration. I am also an admirer of Mr. McKay's own work on the concentration-cells set up in the corrosion of copper alloys.

I fully agree that quantitative work on the action of sulfur dioxide on iron would be profitable; the present work was designed simply to show the effect of altering the concentration of water vapor in the atmosphere on the rate of rusting by sulfur dioxide; the concentration of sulfur dioxide itself was not measured.

I agree with Mr. Hine that the corrosion set up by droplets of water condensed on zinc is due to differential aeration. I have elsewhere[41] studied in some detail the action of drops of water on iron and steel, and I may add that I have noticed similar effects where the drops were produced by the condensation of water vapor on the iron. I do not doubt that condensation on zinc would produce analogous results.

Mr. Parsons' work on aluminum bronze interests me very much, as it is in close agreement with my own results on other materials.[42] I should certainly expect that in an acid solution a duplex structure would be needed for the production of a sensible differential-aeration current, as indeed Mr. Parsons has found. In neutral solutions, on the other hand, where an oxide-film, often visible, can be produced on the aerated portion, a duplex structure is not usually needed.

I am interested in the conclusions reached as a result of the discussion between Dr. Saklatwalla and Mr. McKay, namely, that there is no sharp distinction between big-scale electrolytic corrosion, with large, well-defined anodic and cathodic areas, and currents flowing over considerable distances, which can be tapped and roughly measured, and electrochemical corrosion on an ultramicroscopic scale, in which we can imagine the anodes and cathodes to be contiguous molecules. I myself once ventured[43] to go even further, and to suggest that "chemical corrosion" could be regarded

[41] J. Soc. Chem. Ind., 43, 315 T (1924).
[42] Described in Chem. Met. Eng., 30, No. 24 (1924).
[43] Metals and Metallic Compounds, Vol. I, p. 425 (1923).

as electrochemical corrosion in which the anodic and cathodic reactions took place on the same area.

But, while fully agreeing that all chemical action has an electronic basis, I think as a result of more recent work that we may usefully distinguish between cases where the metal passes, temporarily or permanently, into the ionic condition, from those in which no ions are produced. Thus in the electrochemical attack of sodium chloride upon zinc, the metal passes into the ionic condition at the anodic areas yielding zinc chloride, while sodium hydroxide is produced at the cathodic areas; where the zinc chloride meets the sodium hydroxide, they interact, yielding a precipitate of zinc hydroxide, but since this is formed a short way from the metal surface, it will not protect the zinc from further corrosion. On the other hand, the direct attack of oxygen, as when a metal is heated in air, will produce a film of oxide in close contact with the metal, which will usually tend to interfere with further attack.

Recent work on differential aeration has indeed emphasized the distinction between the two kinds of attack. On the aerated area a film of oxide is produced, and in the case of lead, copper, brass and zinc, the presence of this film can be recognized by the appearance of interference colors. The film ennobles the metal covered, and protects it from corrosion; but by raising the potential of the area so covered, it causes anodic attack to occur at any places which have not received this protective oxide-film, and at such places the metal passes into the ionic condition.

In a case like that, tarnishing or direct oxidation is characteristic of the aerated, cathodic areas, and corrosion is characteristic of the unaerated, anodic areas. There may, of course, be exceptions. As Mr. Vernon truly points out, there are cases where continued direct attack may lead not to the increase of weight, but to a decrease of weight, owing to the flaking off of the skin produced; he is also right in saying that there are cases of acknowledged electrochemical corrosion where the products happen to stick to the metal surface in the early stages; but, in general, it seems to me profitable to regard tarnishing and corrosion as being the converse of each other, rather than as different manifestations of the same phenomenon.

I am glad to find, however, that the differences which exist between Mr. Vernon and myself are mainly questions of nomen-

clature and classification. I would have no objection to adopting the word "surrosion" if I thought there was a reasonable chance of its employment becoming general. As regards the question of the employment of the word "catalysis" in cases where the function of the so-called catalyst is merely to bring the reacting substances together, I do not think that this extension of the meaning would be advisable, since it would then be necessary to regard a glass stirring rod as a catalyst.

Mr. Vernon asks my opinion regarding the action of water vapor in restraining the tarnishing of copper by a low concentration of hydrogen sulfide. The first of the explanations suggested by him closely accords with that which I have adopted in the paper. For rapid tarnishing it is advisable to cut down the proportion of oxygen to the theoretical amount, so as to produce the formation of a pervious and therefore rapidly thickening sulfide-film, instead of an impervious and slowly thickening oxide-film. In the presence of large amounts of hydrogen sulfide a thin film of water, by cutting down the oxygen-concentration, stimulates tarnishing; but if the hydrogen sulfide is only present in the air in small traces, the water may interfere unduly with its access to the copper and thus restrain tarnishing. But I have only put forward this explanation tentatively, because I recognize that further work on the effect of varying the concentrations of hydrogen sulfide, water and oxygen would be needed before we can be confident on this point.

A paper presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 2, 1924, Dr. Saklatwalla in the Chair.

THE INFLUENCE OF EMULSOIDS UPON THE RATE OF SOLUTION OF IRON.[1]

By J. Newton Friend,[2] D. W. Hammond[2] and G. W. Trobridge.[2]

Abstract.

Emulsoids or protective colloids exert a very pronounced retarding influence upon the rate of corrosion of iron. This retardation is due to the adsorption of the emulsoid. A possible method is suggested of treating natural and other waters, to render them less corrosive towards ferrous and non-ferrous metals in practice. In the experiments recorded, small plates of steel were suspended in solutions of lead acetate, to which small measured quantities of agar were added. The results show a marked retarding action of the agar with rise in concentration. Other steel plates were suspended in solutions of copper sulfate, containing in turn 0.05 per cent of one of a series of emulsoids. Again the emulsoids showed a pronounced retarding influence. The deposition of copper on the surface of the plate affords only little protection to the underlying metal. The corrosion loss increases with the temperature; the percentage retardation, due to the emulsoid, at first slightly rises with the temperature, but then falls. In dilute sulfuric acid and stationary plates, the retarding effect is readily detected. However, if the plates (as discs) are rapidly rotated, little protective effect is observed. Iron cooking utensils resist corrosion remarkably well. This may be attributed in part to the protective action of the colloidal food material which is cooked in these utensils. [C. G. F.]

In 1921 attention was directed to the very pronounced retarding influence exerted by emulsoids or protective colloids upon the

[1] Manuscript received July 7, 1924. The word iron is here used in its chemical sense, and refers to any form of the metal, whether steel or wrought iron.

[2] Corrosion Research Laboratory, Municipal Technical School, Birmingham, England.

rate of corrosion of iron.[3] It was further observed that when the various emulsoids were graded according to their powers of inhibiting corrosion, the order was closely similar to that found by Iredale[4] for their retarding influence on the catalytic activity of colloidal platinum towards hydrogen peroxide. It is not difficult to trace a relationship between this and Zsigmondy's "Gold Numbers" for the particular emulsoids tested. It was subsequently shown, in three later contributions[5] to the subject, that protective colloids similarly retard the dissolution of metals in acid, the corrosion of non-ferrous metals such as zinc and lead, the rate of dissolution of salts in water, and several other like reactions. Indeed, the results appeared to warrant the enunciation of a general law of retardation, according to which EMULSOIDS TEND TO RETARD THE VELOCITY OF SUCH REACTIONS, WHETHER CHEMICAL OR PHYSICAL, AS INVOLVE A CHANGE OF STATE FROM SOLID TO LIQUID, OR VICE VERSA, IN ONE OR MORE OF THE COMPONENTS.

This retardation was shown to be due to adsorption. For, although it is not easy to determine quantitatively the minute amount of emulsoid that would be adsorbed by the solid surfaces in the reactions mentioned above, it is reasonable to suppose that it would be an amount directly proportional to the retardation. Hence, the adsorption law may be written as—

$$R = K \sqrt[n]{C}$$

where K and n are constants, C is the percentage concentration of the emulsoid, and R is the percentage retardation. When the logarithm of the retardation was plotted in the usual manner against the logarithm of the concentration, the resulting curves approximated to straight lines in the majority of cases, provided the concentration of the emulsoids was not too low, and thus conformed to the requirements of the adsorption law. One notable exception was the retardation of the rate of solution of certain salts in water. This distinctly did not follow the adsorption law,

[3] Friend, J. Chem. Soc., **119**, 932 (1921).

[4] Iredale, *ibid.*, **119**, 109 (1921).

[5] Friend and Dennett, J. Chem. Soc., **121**, 41 (1922); Friend, Nature, **109**, 341 (1922); Friend and Vallance, J. Chem. Soc., **121**, 466 (1922).

but this was undoubtedly due to a "salting out" of the emulsoid at high concentrations, a result to be expected.

The study has now been considerably extended, and it is gratifying to note that the results are in perfect harmony with those previously obtained, and fully confirm the retardation law as enunciated in 1922.

At the suggestion of Dr. Saklatwalla, we have ventured to give a brief description of our experiments, insofar as they concern the corrosion and dissolution of iron, for they have not hitherto received publication, and it is thought that they may be of interest as suggesting a possible method of treating natural and other waters, to render them less corrosive towards ferrous and non-ferrous metals in practice.

CORROSION OF IRON IN LEAD ACETATE SOLUTION.

In these experiments small plates of mild steel, measuring approximately 4 x 5.5 sq. cm. in area, were suspended by glass hooks in solutions of lead acetate in beakers of 600 cc. capacity, and containing 500 cc. of solution. These were maintained at constant temperature in thermostats of the usual type. Prior to introduction into the solutions, the plates had been freed from scale by soaking in dilute acid, after which they were washed in water, soaked in dilute caustic soda, again washed and dried. They were finally polished with emery paper and weighed. This procedure has been found to yield the most satisfactory results.

In most corrosion experiments, it is usually regarded as sufficient to determine the loss in weight of the suspended metal by direct weighing. If, however, any deposit which is difficult to detach should form upon the surface of the metal this method may yield either too low or too high a result, according to whether the deposit is incompletely removed or, upon complete removal, carries away with it superficial layers of the unattacked metal physically adhering to it.

It was of interest to determine, therefore, whether or not a quantitative estimation of the iron in solution, at the conclusion of an experiment, agreed with the loss in weight of the metal as obtained by direct weighing. To this end plates of steel were suspended in 0.5 per cent lead acetate solution, either free from or containing 0.05 per cent of agar, for 73 hours at room tem-

perature, after which they were removed, washed, dried and reweighed. The washings were added to the lead acetate solutions, and the total iron dissolved was estimated gravimetrically by precipitation and weighing as Fe_2O_3. The results are recorded in Table I.

TABLE I.

Plate No.	Lead Acetate Per cent	Agar Per cent	Loss in weight of plate, g.	Weight of iron in solution, g.
1	0.5	....	0.4578	0.4512
2	0.05	0.05	0.3706	0.3661
3	0.5	0.05	0.3652	0.3619

These results are interesting in that they show:

1. The degree of accuracy that may be expected in "repeat" results for reactions of this type.

2. That even such low concentrations as 0.05 per cent of agar reduce the velocity of the reaction by some 20 per cent.

3. The loss in weight of the metal as determined by drying and weighing gives a result sufficiently accurate for the purpose in hand.

TABLE II.

Loss in Weight of Steel Plates.

After suspension for 70 hr. in 0.5 per cent lead acetate solutions, at 10° C.

Emulsoid 0.05 per cent	Loss in weight g.	Relative Corrosion	Loss in weight of passive plates, g.
———	0.3928	100	0.0086
Sucrose	0.3828	98	0.0044
Egg Albumin	0.3398	86	0.0090
Gum Acacia	0.3182*	81	.....
Dextrin	0.3170	80	0.0032
Agar	0.2994	76	0.0042
Gelatin	0.2064*	52	.....

* Mean of two results.

Experiments were then carried out with similar concentrations, namely, 0.05 per cent of other emulsoids in 0.5 per cent lead acetate solution. The results showed good concordance, provided the metal did not become passive. On several occasions, how-

ever, for no reason that could be assigned, the plates became passive and showed practically no loss in weight. If only it were possible to induce this passive state permanently at will, many of our difficulties with regard to excessive corrosion would be surmounted. The results are summarized in Table II, the emulsoids being ranged in the order of increasing protective efficiency.

Experiments were next carried out with varying quantities of agar in order to determine whether or not the adsorption law was obeyed. The results are given in Table III.

TABLE III.

Loss in Weight of Steel Plates.

Suspended in 0.5 per cent solutions of lead acetate.

Agar, per cent	0.0	0.01	0.02	0.04	0.10	0.20
Loss in weight of plates in grams*	0.3094	0.2902	0.2526	0.1661	0.1212	0.1399
Relative corrosion	100.0	93.8	81.6	53.7	39.2	45.2
Retardation per cent† ..	.....	6.21	18.35	46.3	60.8	54.8

* Mean of two results.

† Calculated from the formula:

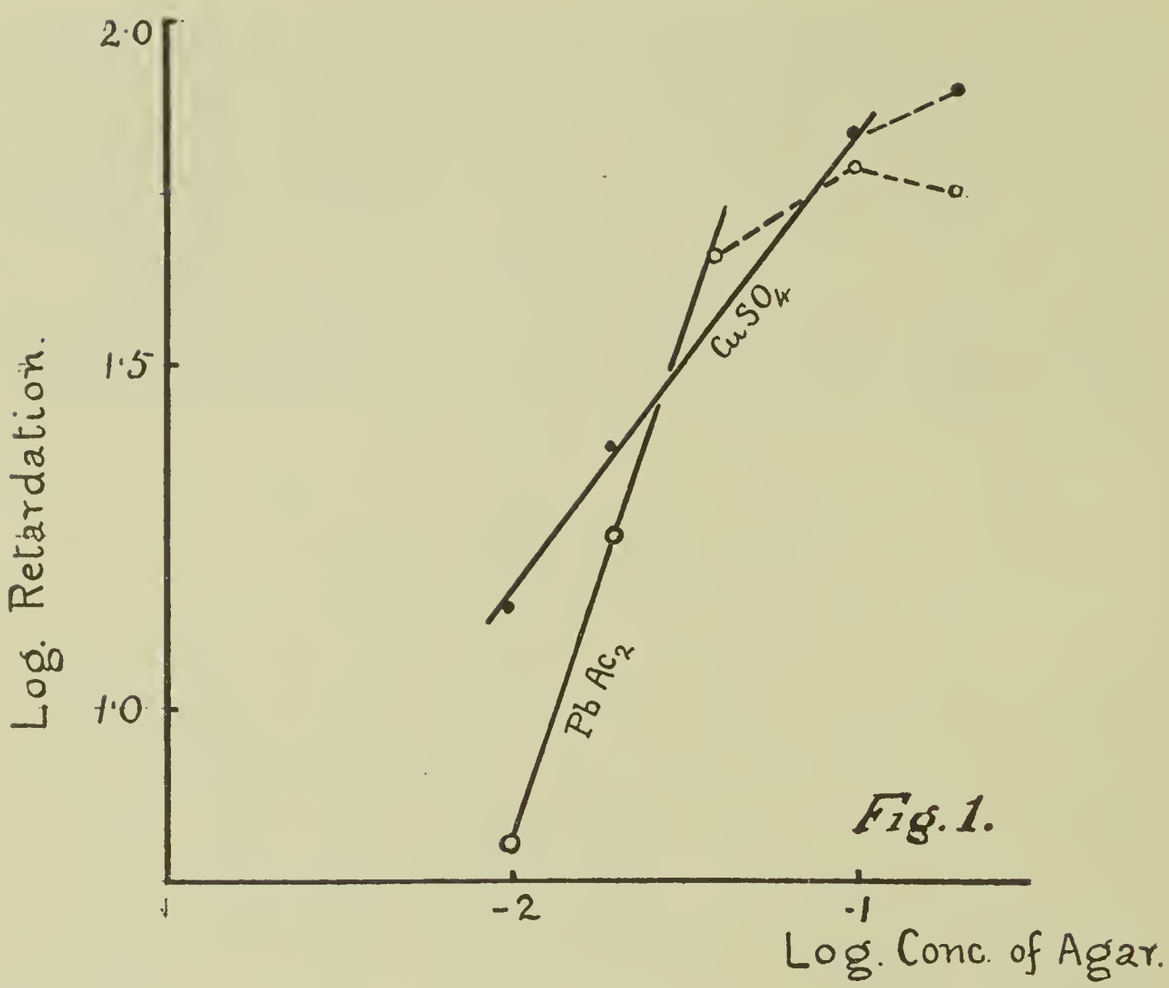
$$100 \times \frac{\text{Loss in Wt. without Colloid} - \text{Loss in Wt. with Colloid}}{\text{Loss in Wt. without Colloid}}$$

or 100 — Relative Corrosion.

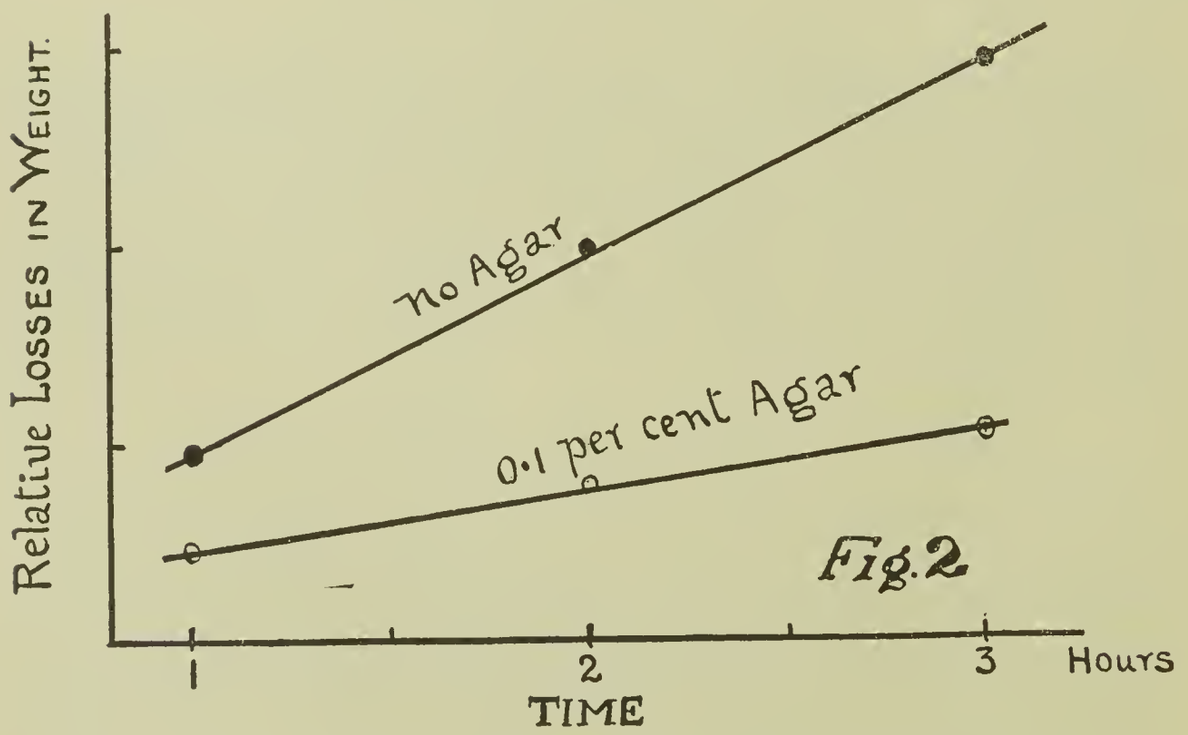
These results illustrate the marked retarding action of the agar with rise of concentration. In Fig. 1 the data are plotted logarithmically in the manner already explained. They do not conform satisfactorily to the requirements of the adsorption law at the higher concentrations, possibly on account of some disturbing action caused by the acid radical, but the lower concentrations appear to obey the law.

CORROSION OF IRON IN COPPER SULFATE SOLUTION.

These experiments were carried out with plates of mild steel in a precisely similar manner to the preceding series, the concentration of the copper sulfate solution being uniformly one per cent. In no case was any tendency towards passivity observed, and it was therefore possible to study the influence of the emulsoids somewhat more thoroughly.



Dilute solutions of agar retard the dissolution of steel in solutions of copper sulfate and lead acetate, in accordance with the adsorption law.



Rate of solution of steel plates in 1 per cent copper sulfate solutions, at 80° C.

In the first series of experiments the effect of adding 0.05 per cent of different emulsoids was studied. The plates were immersed in the solutions for 22 hours at 11° C. and their losses in weight determined. The results are given in Table IV.

TABLE IV.

Loss in Weight of Steel Plates.

After immersion for 22 hr. in 1.0 per cent copper sulfate solution, at 11° C.

Emulsoid 0.05 per cent	Loss in weight in grams*	Relative corrosion	Relative corrosion in lead acetate solution Table II	Relative corrosion in aqueous solutions†
———	0.6571	100	100	100
Sucrose	0.6630	101	98	112
Albumin	0.6011	91	86	7
Dextrin	0.5876	89	80	55
Gum Acacia	0.5823	88	81	57
Gelatin	0.5578	85	52	41
Agar	0.2116	32	76	3

* Mean of two results each.
† With 0.2 per cent of emulsoid. Mean of two results each.

TABLE V.

Loss in Weight of Steel Plates.

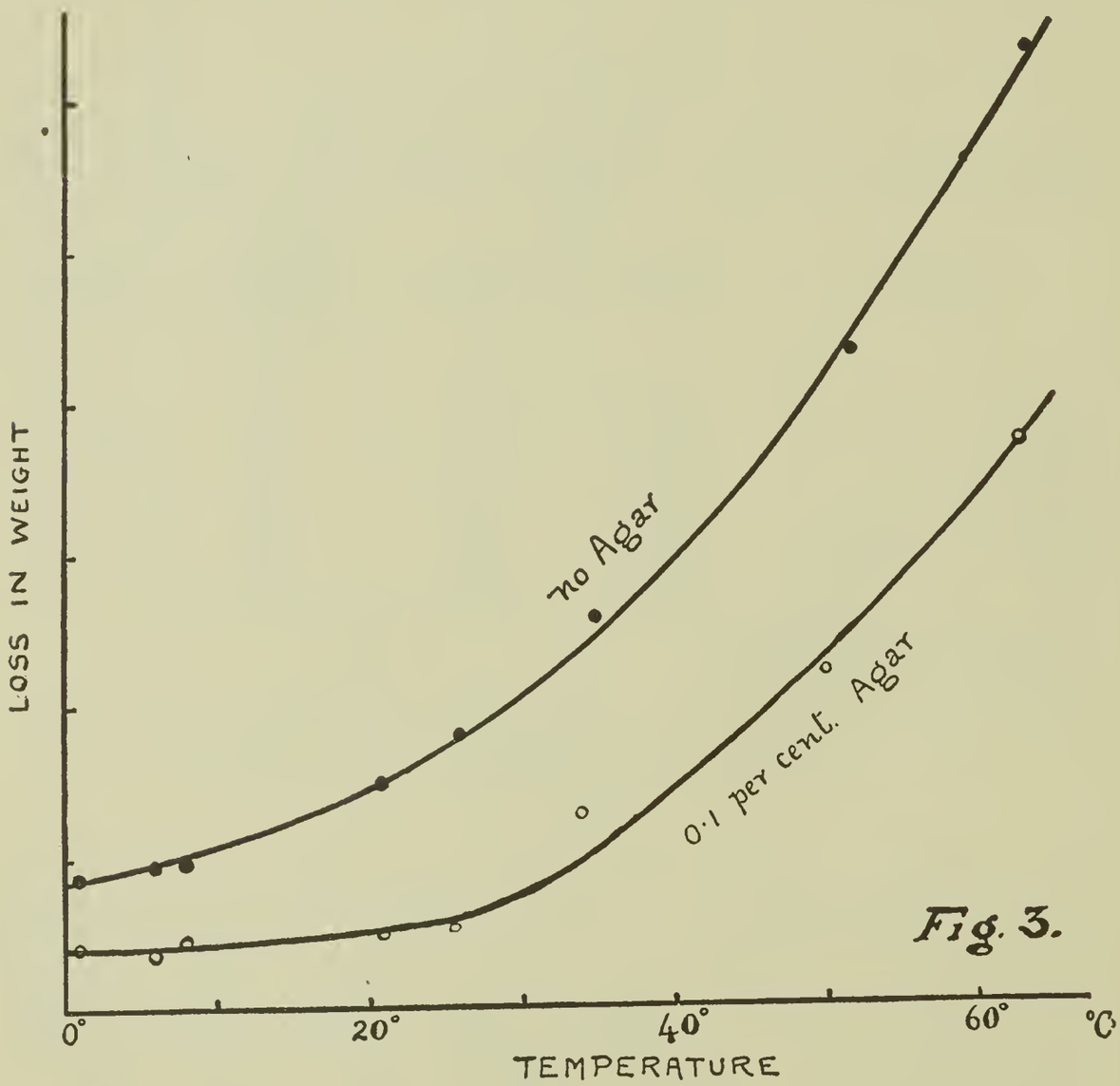
After immersion for 22 hr. in 1.0 per cent copper sulfate solutions at 13° C.

Agar, per cent	0.00	0.01	0.02	0.10	0.20
Loss in weight grams* ..	0.6815	0.5852	0.5195	0.2256	0.1392
Relative corrosion	100.0	85.8	76.2	33.1	20.4
Retardation per cent† ..	.....	14.1	23.8	66.9	79.6

* Mean of two results.
† See footnote to Table III.

For the sake of easy comparison, the results obtained with lead acetate solutions listed in Table II, and in pure aqueous solutions containing 0.2 per cent of emulsoid, as found by Friend and Vallance in 1922, are included in Table IV. It will be observed that, with the exception of gelatin and egg albumin, the order of the inhibiting actions of the emulsoids is substantially the same.

Gelatin is known to be erratic, and decomposition of the albumin on prolonged standing (namely, three weeks) in the distilled water suffices to account for the abnormality manifested by this emulsoid.



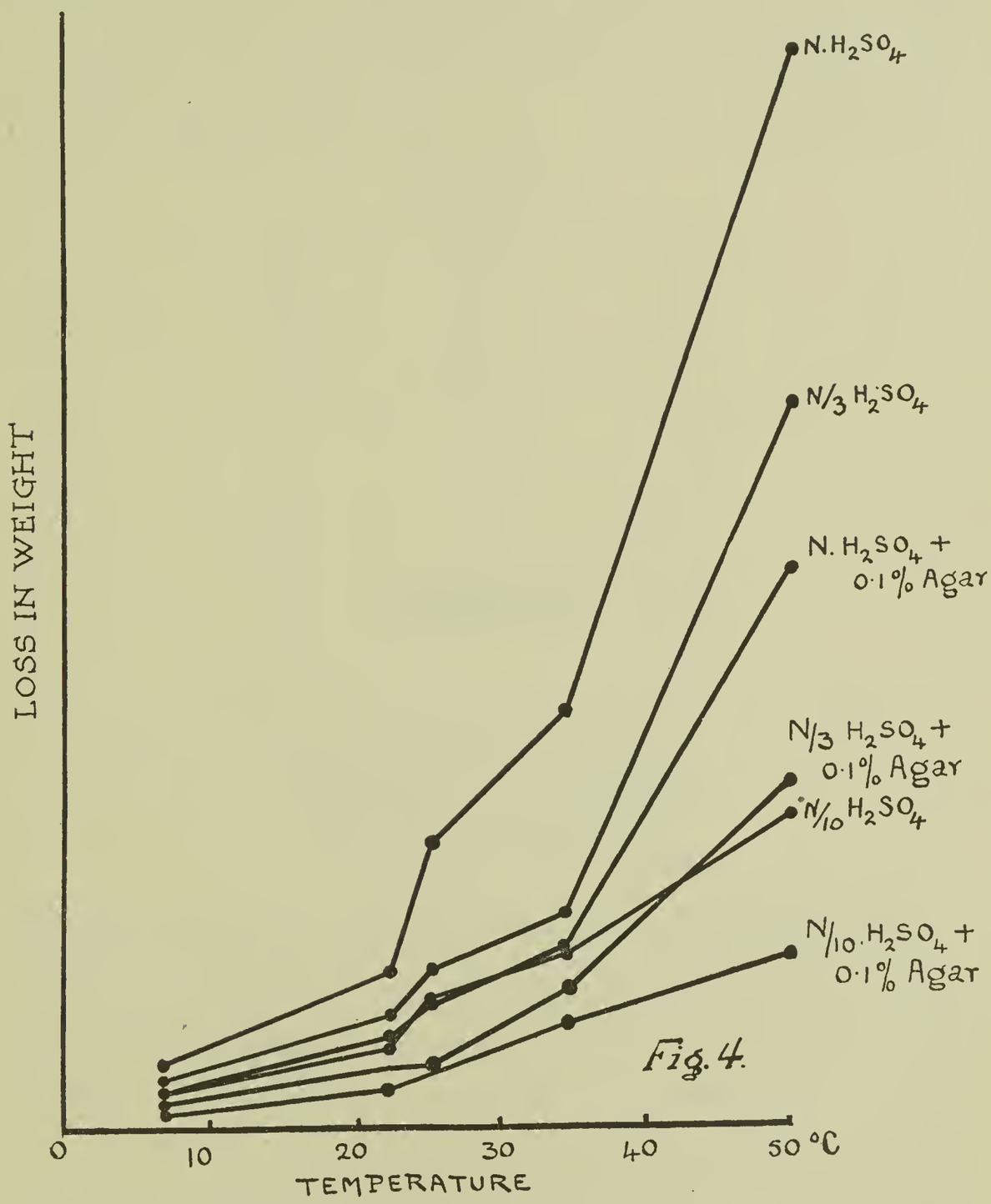
Influence of temperature upon the rate of solution of steel in 1 per cent copper sulfate solutions.

Experiments were next carried out with varying quantities of agar in one per cent solutions of copper sulfate, in order to determine whether or not the adsorption law was obeyed. The results are given in Table V.

These results are shown graphically in Fig. 1, and are seen to agree quite well with the requirements of the adsorption law for the lower concentrations.

The results of experiments carried out with the object of de-

termining the combined influence of rise of temperature and increase in duration of the experiments are shown graphically in Fig. 2 and 3. The rate of solution of the iron is practically a



The solubility of iron in dilute solutions of sulfuric acid at various temperatures.

linear function of the time, during the first three hours at room temperature (Fig. 2). Evidently the deposition of copper on the surface of the plate affords little protection to the underlying metal. From Fig. 3, which shows the results obtained in experi-

ments of one hour's duration, with and without 0.10 per cent of agar, it is evident that the percentage retardation as defined by the foot-note to Table III at first slightly rises with the temperature, but afterwards falls. This is evident from the following data calculated from the smoothed curves:

Temperature ° C.	1	8	21	35	50	65	80
Retardation per cent	54	54	71	57	45	37	31

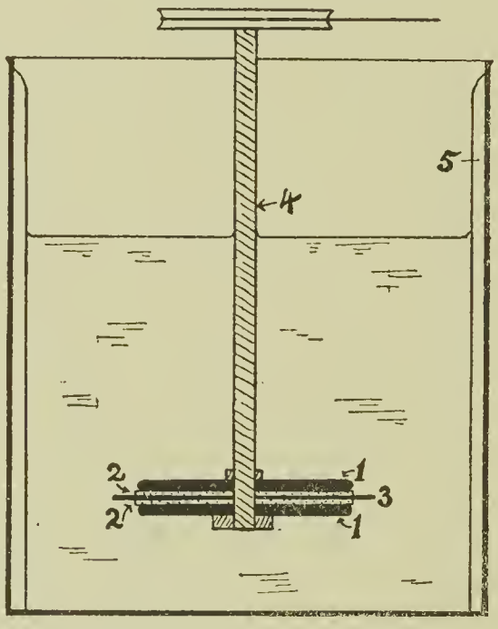


FIG. 5. Apparatus to determine the influence of rotation upon the rate of solution of iron in acid. 1. Mahogany disc. 2. Xylonite disc. 3. Electrolytic iron foil. 4. Bronze shaft, protected with collodion. 5. Internal rib in the glass.

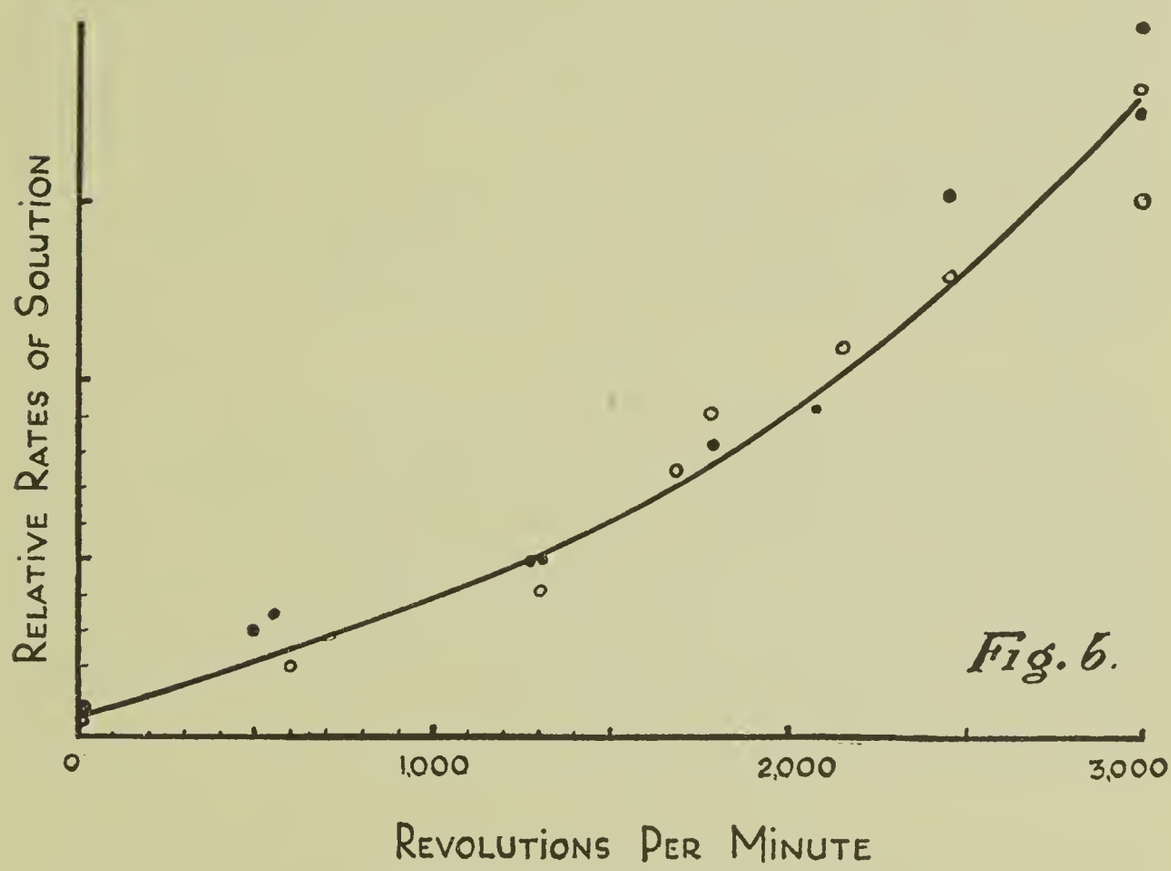
This is important as showing that substances, which yield satisfactory protection to metals at ordinary temperatures, will not necessarily prove so efficient at high temperatures. Opportunity may be taken, therefore, to emphasize the need of carrying out all tests on corrosion in the laboratory under conditions approximating as closely as possible to those obtaining in practice, if results of practical value are to be obtained.

Despite the deposition of copper on the steel, the rate of solution rises regularly and rapidly, the temperature curve (Fig. 3) closely resembling that for iron corroding in tap water at various temperatures.[6]

[6] Friend, Carnegie Scholarship Memoirs of the Iron and Steel Institute, **11**, 1-156 (1922).

RATE OF SOLUTION OF IRON IN DILUTE SULFURIC ACID.

The rate of solution of mild steel in dilute sulfuric acid has been determined by immersing the plates in about 800 cc. of solution and noting their loss in weight after given intervals. The retardation produced by 0.1 per cent agar is pronounced, and reaches a maximum at 25° C. in all three concentrations of acid. The results are shown in Fig. 4.



Influence of rotation upon the rate of solution of iron in dilute sulfuric acid. Dots indicate $N/10$ sulfuric acid; circles, $N/10$ sulfuric acid with 0.1 per cent agar.

If the curves were rounded off, they would clearly be of the usual parabolic type, so frequent for corrosion-temperature diagrams.

RATE OF SOLUTION OF RAPIDLY MOVING IRON IN DILUTE SULFURIC ACID.

In 1922 it was shown[7] that by rotating discs of pure iron foil in solutions of dilute sulfuric acid, the rate of solution of the metal was a linear function of the velocity of rotation. The apparatus used in the present experiments was slightly modified,

[7] Friend and Dennett, J. Chem. Soc., **121**, 466 (1922).

the disc of iron being protected, except at the rim, by xylonite discs kept flat with thicker discs of mahogany (Fig. 5).

The glass jar contained 1,500 cc. of $N/10$ acid, its capacity being 2,500 cc. The inside of the jar was ribbed vertically, a device that greatly reduced the tendency of the liquid to swirl around with the disc. The jar was immersed in a thermostat at room temperature (14° C.). A 0.25 h. p. motor was used, and velocities up to 3,000 revolutions per minute were readily attained, corresponding to a velocity of about 52 miles per hour. It seemed interesting to determine whether or not small quantities of agar would retard the solution of iron under these conditions. The results, shown graphically in Fig. 6 indicate that little protective effect is observed. Presumably the violent mechanical agitation tends to destroy the completeness of the adsorbed layer.

FINIS.

The foregoing results are not without practical interest. Cooking utensils are well known to resist corrosion remarkably well, and this may be attributed in part to the protective action of the colloidal food material which is cooked in them. Many of the substances recommended for the prevention of corrosion of boilers are emulsoid in character, and no doubt their protective action is due in like manner to adsorption.

DISCUSSION.

Wm. Blum[8]: In recent years a large number of plants have made various colloidal additions to the pickling baths for the purpose of producing more uniform pickling. Their evident object is to reduce the rate of solution of the metal, that is, the iron in the acid, while leaving the rate of the solution of iron oxide unchanged. This use suggests the possibility that the effect may not be due simply to adsorption, as assumed by Dr. Friend, but may also be due to the direct migration of the emulsoid.

If we assume that in pickling there is electrochemical action. with finite distances between the anodic and cathodic portions, the emulsoid, such as gelatin, will migrate to the cathodic areas and

[8] Chemist, Bureau of Standards, Washington, D. C.

will tend to retard the evolution of hydrogen there, which must accompany metal solution at anodic points. If such an effect enters, it could perhaps account for the effect of agitation. If it is purely a matter of adsorption, a more uniform concentration of the emulsoid is maintained at the metal surface when the solution is agitated, and, therefore, we would expect an equal or greater degree of adsorption than if the solution were still, somewhat impoverished by the adsorption. If, however, electrochemical action causes the migration of the emulsoids to certain areas of the metal, agitation will tend to reduce its concentration and to counteract its protective effect.

R. J. McKay[9]: On page 285 the conditions of the experiment are described, but there is no description or mention of analysis of oxygen in the solution, nor of possible velocity effects from heating in the thermostat. The temperature is controlled apparently carefully, but the oxygen and the supply of oxygen to the surface, which we know is of much more fundamental importance in corrosion, is apparently quite uncontrolled. That this has an important bearing on the results is shown by the draft given on page 293, where the comparatively high velocities have much lessened the effect of the emulsoid, if not removed it altogether. It would be well worth while if Dr. Friend could give us figures on the actual conditions existing when the emulsoids show a large effect, and the limits of these conditions.

J. A. Parsons[10]: In preparing the samples, on page 285, Dr. Friend refers to a preliminary acid dip. The question has occurred to me whether or not such acid pickling would tend to produce an abnormal charge of hydrogen on the surface, thus affecting the corrosion rate. In testing samples of high silicon irons, we have found that, for a given set of conditions, unpickled samples give more consistent results in a given series than pickled ones.

F. N. Speller[11]: Relatively, the results would be the same, I should say, if the samples are all treated the same. The effect of pickling would naturally increase the area exposed, tending to increase the initial rate of corrosion. On the other hand, if there

[9] Supt. Technical Service, International Nickel Co., New York City.
[10] Experimental Engr., Duriron Co., Dayton, Ohio.
[11] Metallurgical Engr., National Tube Co., Pittsburgh, Pa.

is any hydrogen left on the surface, it would tend to decrease the initial rate, but the ultimate result would probably be the same in any one series of experiments covering a sufficient period of time. The loss during the first 48 hours might show marked inconsistencies, due to these factors.

R. J. McKay: Dr. Friend has shown, on page 284, that the data correspond with the adsorption law, and draws the conclusion, therefore, that this effect of emulsoids is entirely due to adsorption. Is it not possible that the effect of the emulsoids might also be due, at least partially, to their effect on the rate of diffusion of the corrosion products to the surface? Would it not be necessary to show that the data do not correspond with the diffusion laws, before drawing his conclusion?

J. Newton Friend (*Communicated*): In reply, I wish to express my appreciation of the kind manner in which my paper was received. Since writing it I have seen the interesting paper by Whitman, Russell, Welling and Cochrane,[12] and was pleased to note that my curve on page 293 bore a close resemblance to the oxygen curve in Fig. 3 of the above-mentioned paper.

In reply to Messrs. Blum and McKay, while not ruling out other auxiliary actions, I think that the results indicate adsorption to be the *main* factor in retarding the corrosion in the experiments concerned.

In reply to Mr. McKay, the solution in the velocity tests was so vigorously churned that it was continuously milky with bubbles, and was probably saturated with air the whole of the time.

In reply to Mr. Speller, I should like to draw attention to the fact that, after the acid wash, the plates were neutralized with dilute alkali, washed and finally polished with emery paper. Experience has shown that this treatment tends to remove most of the disturbing factors induced by the acid, and the plates so treated yield results quite as uniform among themselves as those prepared by any other process I have tried.

[12] J. Ind. Eng. Chem., **15**, 672 (1923).

A paper presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 2, 1924, Dr. Saklatwalla in the Chair.

THE "STAINLESS" CHROMIUM STEELS.[1]

By W. H. Hatfield.[2]

Abstract.

The presence of chromium when added to steel results in an increased passivity in the presence of nitric acid; yet on the other hand, as shown by the author, the solubility in hydrochloric acid, and particularly in sulfuric acid, is increased in the case of the steels rich in chromium. Such facts indicate the complexity of the subject when the data are studied with a view to formulating helpful and satisfactory laws to guide further experiment. There is evidence that the presence of chromium under strongly oxidizing influence permits of the immediate modification of the surface of the metal, in such a way as to produce complete passivity under certain conditions of temperature and concentration of the corroding media. The influence of corroding media is readily modified by the presence of colloids. In an appendix are listed (1) reagents found to have little or no action on stainless steel, and (2) those reagents which do corrode stainless steel more or less readily.

As the author has already contributed several papers dealing with this subject, which are available elsewhere,[3] it is proposed in this instance to confine the paper to some extremely interesting aspects of the influence of corroding media upon stainless chromium steels. These steels really constitute a range of the ternary alloys of iron, chromium, and carbon,[4] and their industrial importance is essentially due to the presence of the high per-

[1] Manuscript received July 11, 1924.

[2] Brown-Firth Research Laboratories, Sheffield, England.

[3] Proc. Aeronaut. Soc. Great Britain, 1917; Proc. Sheffield Cutlery Trade Soc., Dec. 17, 1919; "The Engineer," Dec. 15, 1922; Trans. Faraday Soc., 19, 159-69 (1923); J. Iron and Steel Inst., 2 (1923); Am. Soc. Steel Treating (Canadian Chapter), May 31, 1924.

[4] See Patent Specifications of Brearley, Haynes, Cox, Krupp and others.

centage of chromium; that is, the well-known non-corrosive properties of the stainless steels could not be produced, whatever the diverse heat-treatment employed, unless the chromium be present in sufficient quantity. Further developments, or the attendant circumstances involved in their production, have led to steels being produced more complex,[5] but based upon the iron-chromium-carbon series, which contain in addition to the chromium, such elements as nickel, silicon, copper, molybdenum, etc. The modification in the properties of steels from the standpoint of corrosion, wrought by the addition of various elements, is of considerable interest. In considering the matter, the data presented in Table I, prepared by the author, relative to the solubility of some of the essential elements in acids, will be of interest.

TABLE I.

Solubility of Metals in Acids.

24 hours' immersion at 15° C. Weight of samples 50 g. The result is given in loss in weight per sq. cm. of surface.

Metal	HCl Conc.	H_2SO_4 10 per cent by vol.	HNO_3 Sp. gr. 1.20 50 per cent by vol.
Iron	—0.0814	—0.0327	—0.7165
Nickel	—0.0037	—0.0002	—0.1546
Chromium	—0.2014	—0.0014	—0.0006
Copper	—0.0018	—0.0002	—0.5708
Cobalt	—0.0480	—0.0150	—0.4210
Manganese	—1.1579	—0.7724	—0.5688
Aluminum	—0.1071	—0.0002	—0.0010
Silicon	—0.0002	—0.0003	—0.0002

It will be noted that the metal chromium is practically resistant to nitric acid; the addition of one-eighth part of this element by weight to the steel confers upon the iron with which it is alloyed in the form of steel, a resistance to that acid over a greater range of concentration and temperature. It will be noted that nickel is resistant to sulfuric acid, and it is of interest to record that 25 to 30 per cent of this element confers similar extended range of resistance to a nickel steel. In other words, the smaller quantity of the added element confers some of its properties upon the

[5] See Patent Specifications of Strauss (Krupp), Saklatwalla, Armstrong, Johnson and others.

metal to which it is alloyed. The author has shown[6] that the addition of nickel to chromium steels gave increased resistance to sulfuric and hydrochloric acids, and also that the addition of chromium to high content nickel steels greatly increased the resistance of a nickel steel to nitric and hydrochloric acids. It is also claimed that the additions of silicon, copper, molybdenum, tungsten, etc., also further modify the chemical properties of the alloys produced.

In the present paper the author will confine himself to the stainless steels, in which 12 to 16 per cent of chromium is the essential alloyed element. These steels have the advantage that whereas stainless or rustless steel, produced by the addition of heavier percentages of alloys, are generally austenitic in character, the straight chromium steels can, with the carbon in the neighborhood of 0.3 per cent, be effectively hardened for the production of cutting implements. They have the further advantage that the presence of the high chromium content raises the carbon change point to over 800° C., by virtue of which fact reasonably hot manipulation can be done without entering the solid solution range of temperature. This is found to be a considerable advantage in industrial processes, whereby the material is applied to various purposes. While, however, the author is essentially dealing with the 12 to 16 per cent chromium steels, he would emphasize the importance of the other corrosion-resisting steels, which are now available, to which the additional elements have been added. Such steels, while more costly, yet fulfill satisfactorily more onerous conditions, that is, they resist corroding media which the ordinary, now well-known stainless steel does not resist. The latter, however, as established by its great success when used for cutlery, turbine blades, and engineering parts, has a sufficiently wide range of resistance to corroding media to fulfil the general requirements of a non-rusting steel.

When one speaks of a rustless or stainless steel, one is naturally expressing oneself broadly. Rustlessness or stainlessness are obviously relative terms. One could not, for instance, hope to produce a steel which would resist all corroding media, but that the influence of chromium is fundamental in the modifications

[6] J. Iron and Steel Inst., **108**, 103 (1923).

wrought in the intrinsic characteristics of the steel is well illustrated by a simple experiment.

If turnings or drillings of stainless steel be placed in one beaker, and turnings or drillings of ordinary carbon steel be placed in another, and cold nitric acid of sp. gr. 1.20 be poured

TABLE II.

Action of Acids Upon Steel.

In each case the immersion is for 24 hours at the temperature stated and the change in weight is given in grams per sq. cm. of surface.

STAINLESS STEEL.

C 0.34 per cent, Cr 13.62 per cent, Mn 0.34 per cent

Temperature ° C.	Sulfuric Acid Conc. per cent by vol.			Hydrochloric Acid Conc. per cent by vol.			Nitric Acid		
	5 sp. gr. 1.082	25 sp. gr. 1.297	50 sp. gr. 1.539	5 sp. gr. 1.011	25 sp. gr. 1.046	50 sp. gr. 1.086	*N*/1 sp. gr. 1.033	50 sp. gr. 1.20	100 sp. gr. 1.42
15	0.0880	0.2558	0.0046	0.0162	0.0536	0.0626	0.0032	Nil.	Nil.
40	0.2902	0.6406	0.0115	0.0851	0.3640	0.6180	0.0015	Nil.	0.0001
60	0.4133	0.8787	0.0187	0.0812	0.4027	0.8066	0.0076	Nil.	0.0005
80	0.4592	0.7199	0.2246	0.1043	0.4326	0.8061	0.0103	0.0005	.....

CARBON STEEL.

C 0.29 per cent, Mn 0.52 per cent

Temperature ° C.	Sulfuric Acid Conc. per cent by vol.			Hydrochloric Acid Conc. per cent by vol.			Nitric Acid		
	5 sp. gr. 1.082	25 sp. gr. 1.297	50 sp. gr. 1.539	5 sp. gr. 1.011	25 sp. gr. 1.046	50 sp. gr. 1.086	*N*/1 sp. gr. 1.033	50 sp. gr. 1.20	100 sp. gr. 1.42
15	0.1353	0.2027	0.0020	0.049	0.1367	0.1842	0.0957	0.6766	0.0007
40	0.4004	0.8226	0.0060	0.0866	0.4088	0.6107	0.2820	0.6538	0.0236
60	0.4495	1.2552	0.0105	0.0879	0.4042	0.8341	0.3215	1.3809	0.3970
80	0.4958	1.2741	0.0112	0.0928	0.4112	0.7355	0.3512	1.7278	.....

into both the beakers, the stainless steel is entirely unaffected, while the ordinary steel is violently dissolved with the emission of nitrous fumes. One might, therefore, say that the distinguishing feature between ordinary and stainless steel is that the former dissolves in nitric acid, while the latter does not. Such, however, will be only a half truth, since if the action of nitric acid upon these steels is carefully studied, it will be found, for instance,

that the ordinary steel drillings are passive, that is, do not dissolve in the concentrated nitric acid, say of sp. gr. 1.42, while if the stainless steel is immersed in very dilute nitric acid, then it is slowly attacked. It is thus clear that when one speaks of the resistance of a steel or alloy to an acid, or indeed to any corroding medium, one must qualify the statement by adding the concentration, temperature, and general conditions of the test. The relative resistance of stainless steel and carbon steel to nitric acid, sulfuric acid, and hydrochloric acid, is illustrated in Table II.

One extremely interesting experiment which the author has described before, consisted of immersing two specimens of this stainless steel (in the hardened and tempered condition, having a Brinell hardness of 220) in 10 per cent (by volume) sulfuric acid solution; one specimen had a newly prepared and polished surface, while the other specimen had been immersed for 24 hours in nitric acid, sp. gr. 1.20, but after the immersion in the nitric acid had had the surface perfectly cleaned. These two cylinders when placed in the 10 per cent sulfuric acid displayed a marked difference, the specimen with the new surface remaining unaffected for a few seconds only, and then gas was evolved freely, while the specimen which had been immersed in nitric acid remained passive for several hours. Having in mind that numerous corrosion tests have indicated that 1.20 sp. gr. nitric acid is without influence upon stainless steel, and undoubtedly has no apparent influence, yet immersion in it, as in this experiment, was definitely shown to have rendered the steel passive in sulfuric acid for a considerable period of time. The only other experimental fact within the author's experience, which matches up this experiment, is that stainless steel after considerable use is apparently more stainless than when first put into service.

Another interesting experience with the stainless steel might be recorded. The author was asked whether the steel would resist mine water containing free sulfuric acid. On laboratory experimental work he would have been inclined to say that the steel would not resist, but on receiving samples of the water for corrosion tests, it was found that although there was free sulfuric acid, yet the steel resisted the influence of the water perfectly. This was found to be due to the fact that the water also con-

tained ferric sulfate. A few experiments were put in hand covering this aspect of the matter which are sufficiently interesting to record. See Table III.

TABLE III.

Action of Mine-water on Stainless Steel

Test No.	$Fe_2(SO_4)_3$ g/L	Free H_2SO_4 g/L	Ratio $\frac{H_2SO_4}{Fe_2(SO_4)_3}$	Action upon hardened stainless steel
1	200	50	1 : 4	Unattacked
2	16	4	1 : 4	Unattacked
3	12	4	1 : 3	Unattacked
4	8	4	1 : 2	Unattacked
5	4	4	1 : 1	Unattacked
6	8	8	1 : 1	Unattacked
7	12	12	1 : 1	Unattacked
8	16	16	1 : 1	Unattacked
9	2	4	2 : 1	Unattacked
10	2	6	3 : 1	Unattacked
11	2	8	4 : 1	Unattacked
12	2	10	5 : 1	Unattacked
13	2	12	6 : 1	Slight attack
14	2	14	7 : 1	Slight attack

It will be noted that the action is dependent upon the $H_2SO_4/Fe_3(SO_4)_3$ ratio, and not upon the actual quantity of active reagent present in the solution. The stainless steel in the hard condition was only attacked when $H_2SO_4/Fe_3(SO_4)_3$ ratio was reached of 6 to 1, whereas stainless steel in the soft condition was affected when it was 1 to 1.

It is clearly necessary that the physical condition of a steel be given every consideration, since the stainless steel may be placed in one of many conditions. For instance, it may be in the hardened condition, it may be in the fully tempered condition, or it may be hardened and tempered to different temperatures and for different periods of time, thus producing a very dissimilar internal structure, and physical condition, as judged by mechanical tests. This aspect of the matter is extremely important, when considering the question of stainlessness, where variations in hardness can readily constitute a determining factor as to whether or not such steel resists a medium without staining.

It is, of course, well known that patches of the oxide of a metal,

such as scale, will accelerate the corrosion of a metal, and stainless steel is no exception to this rule. If any patches, however small, of the scale and oxide produced during manufacture are left on the finally prepared surface, corrosion will be quickly set up in that locality. It is, therefore, imperative, if a satisfactory resistant surface is to be obtained, that a perfectly clean metallic surface be prepared. Included slag and non-metallic inclusions may or may not, but probably will, influence the resistance of steel, and this is largely determined by the composition of the slag and of the non-metallic inclusions. Dirty steel fails to resist some media which are completely resisted by clean steel, *i. e.*, steel which has been properly refined, and in which the non-metallic inclusions, present in small quantity, are of a different composition from the inclusions which are present in larger quantities and of different composition, in steel which has not been properly refined. In attempting, therefore, to study quantitatively the influence of various corroding media on an alloy like stainless steel, the matter becomes extremely difficult, owing to the danger of not being able quantitatively to allow for such influences as the condition of surface, and the presence of foreign matter in the steel. However, if the steel is of the correct composition, and has been properly refined, then, as found within the author's experience, reasonably consistent results can be obtained, even with media in which the effective corroding element or compound is present in small quantity.

When considering the resistance to staining in the case of a table knife, it is quite common to see the statement that a stainless steel blade will not be stained if a spot of vinegar is placed upon it and allowed to evaporate. It is claimed that the mark left by the vinegar can be easily removed by the normal domestic methods employed in washing cutlery. Such a claim is, indeed, a reasonable one. If, however, "vinegar" is studied thoroughly, it will be found that the term is really a generic one, and does not describe a material of fixed and uniform composition and characteristics. This is well illustrated by an experiment in which the author purchased five vinegars in the city of Sheffield, and had them thoroughly analyzed, with the results shown in Table IV. Of these five vinegars, the first four were genuine malt vinegars, which would be known in the trade as No. 24, 20,

22 and 22, respectively. No. 5, however, was obviously an artificial vinegar. It will be seen that, while essentially these vinegars consist of an aqueous solution of acetic acid, they contain acid in variable percentage, ranging from 3.82 to 6.12 per cent. It will be noted that the total solids range from 0.32 to 2.46 per cent, and that the phosphoric acid varies from 0.008 to 0.087 per cent. Other important differences are also to be noted.

TABLE IV.

Composition of Vinegars.

	1	2	3	4	5
Specific gravity at 15°	1.0197	1.0170	1.0132	1.0137	1.0070
	Per cent	Per cent	Per cent	Per cent	Per cent
Total acids (as acetic)	6.12	5.01	5.38	5.44	3.82
Total solids	2.46	2.45	1.29	1.29	0.32
Ash	0.44	0.45	0.15	0.12	0.02
Total nitrogen	0.08	0.08	0.033	0.039	0.016
equal to protein	0.50	0.50	0.20	0.24	0.10
Total SO_3	0.105	0.108	0.108	0.025	0.008
Sodium chloride	0.23	0.24	0.18	0.17	0.02
Phosphoric acid (P_2O_5)	0.031	0.085	0.087	0.035	0.008
Free sulfuric acid	None	None	None	None	None
Ferrocyanides	None	None	None	None	None
Calculated on original solids:					
Nitrogen	0.70	0.80	0.35	0.41	0.26
equal to protein	4.38	5.01	2.19	2.56	1.63
Phosphoric acid (P_2O_5)	0.27	0.83	0.94	0.37	0.13

It will thus be seen that it is reasonable to infer that a stainless knife in a certain condition of a particular heat-treatment might resist one class of vinegar, while being stained with another. If, therefore, one speaks of the resistance of stainless steel or any other metal to vinegar, one should be careful to specify the type and quality of that vinegar.

Vinegar is essentially acetic acid in water, and one of the interesting facts which the author has encountered in this field is that there are conditions of stainless knives which will resist a large range of vinegars, but which are immediately attacked by acetic acid of similar strength. He considers that the explanation of this is, that there is an organic colloid in the vinegar, which is instrumental in rendering the steel passive. There are two other

similar cases which the author has experienced, namely, sour milk and lemon juice. It is, of course, well known that lactic acid is an essential constituent of sour milk; stainless steel successfully resists corrosion in the presence of sour milk, but curiously is attacked by lactic acid. Lemon juice does not attack stainless steel, but weak solutions of citric acid in water may do so. It is, therefore, to be inferred that the explanation given in the case of vinegar, probably applies also to the latter two instances.

CONCLUSIONS.

Numerous experiments have shown the 12 to 16 per cent chromium steel to be resistant to many influences. As indicative of those which the steel will resist and those which it will not resist, the appendix will be found of interest.

It is interesting to note that whereas the presence of chromium when added to steel results in an increased passivity in the presence of nitric acid, yet, on the other hand, as shown by the author,[7] the solubility in hydrochloric acid, and particularly in sulfuric acid, is increased in the case of the steels rich in chromium. The action in the case of the sulfuric acid is of particular interest, since while the increased passivity in nitric acid is what one would expect from the characteristics of chromium in this respect, and the increased passivity of high nickel alloys in sulfuric acid is in line with what we would expect from the characteristics of nickel, yet from the characteristics of chromium, which is much less soluble in sulfuric acid than iron, one would, arguing on the premise of the foregoing, expect decreased solubility in sulfuric acid, as a result of alloying the chromium with the steel. Such facts indicate the complexity of the subject when the data are studied with a view to formulating helpful and satisfactory laws to guide further experiment.

When considering the theoretical side of corrosion, one must bear in mind that the chief agent of corrosion is the oxidizing influence of the atmosphere. Resistance to nitric acid is experimentally demonstrated to be an excellent indication of resistance to atmospheric attack. The high chromium stainless steel, however, while extremely resistant to pure atmospheric effects, ap-

[7] J. Iron and Steel Inst., 108, 103 (1923).

pears to be, generally speaking, unable to resist those media which are responsible for reactions in which hydrogen can be, either directly or indirectly, replaced by iron and chromium, although this is not invariably so.

In the appendix is given a brief statement of the result of experiments to date, which have been made in the Brown-Firth Research Laboratories, with a view to determining the resistance, or otherwise, to various corroding media, and it will be seen that it is safe to state that a heat-treated steel containing 12 to 16 per cent of chromium is intrinsically made more resistant by the addition of that element, and that its resistance extends over a wide range of corroding media. It is not by any means clear what the mechanism of this action is, but the author considers that there is evidence that the presence of chromium under strongly oxidizing influences permits of the immediate modification of the surface of the metal in such a way as to produce complete passivity under certain conditions of temperature and concentration of the corroding media. The experiment detailed in the paper in which the preliminary immersion in nitric acid extended the period of passivity in sulfuric acid supports this view.

The influence of corroding media is readily modified by the presence of colloids, and the cases of vinegar, lemon juice, and sour milk would appear to support this view, since the isolated acids in each case attack the steel. There is evidence also of another kind which points in this direction, namely, that the organic restrainers used in the acid pickling of ordinary carbon steels undoubtedly will, if added in a critical percentage, prevent the solution of the steel in the acids.

There are many anomalies in the experimental field associated with the developments of rust-resisting steel, several of which the author has endeavored to describe in this paper; many others no doubt yet remain to be discovered. Although it may be desirable to have a satisfactory working theory, he is of the opinion that at the present time much further experimental work is necessary, and a much more complete agreement is also necessary between the chemist and the physicist, concerning the mechanism of the action whereby elements and combinations of elements react one with another, before the fundamental laws can be convincingly postulated.

In conclusion the author desires to thank the directors of Messrs. Thos. Firth & Sons, Ltd., of Sheffield, for permission to publish data and information resulting from investigations carried out on their behalf.

APPENDIX.

Media Satisfactorily Resisted.

Absolute alcohol, acetone vapor, aerated water, ammonium hydroxide, ammonia liquor, ammonium nitrate, apple juice, "azol," beer, benzene (petrol mixture), Benger's food, benzol, bleaching solution, blood, boric acid, brewing materials, calcium hypochlorite, cane sugar molasses, carbolic acid, caustic soda solution, chocolate, cider, claret, colliery waters (some), copal varnish and graphite, cylinder oil, drains, ethyl chloride, formaldehyde, fruit juices, glycerine, hydrokinone developer, inks (some), "kodak" developer, lemon juice, lime and limestone (emulsion in water), liqueur brandy, lubricating oils, lysol, mercuric cyanide, mercuric iodide, metol (hydrokinone developer), milk (fresh), milk (sour), nitric acid (above sp. gr. 1.062), novocaine, oleic acid, onions, orange juice, oxo, paraffin, petrol, port, potassium carbonate, potassium cyanide, potassium nitrate, potassium oxalate, pyro-soda developer, reservoir water, river water, "rytol," sauces (table,) sewage (general), sherry, sodium bicarbonate, sodium hypochlorite, sodium phosphate, sodium salicylate, soft soap, stearic acid, sugar solution, tan extract (leach liquor and finished extract), tannic acid, tartaric acid, tomato, uric acid, urine, vinegar (malt), whisky, wood (a) greenheart, (b) oak.

Media Not Resisted.

Acetic acid vapor, acetic anhydride, acetone, alum, aluminum sulfate, ammonium chloride, ammonium sulfate, aqua regia, bromine, calcium chloride, carbon tetrachloride, caustic soda (anhydrous) at 550° C., chloracetic acid, chloric acid, chlorine, chlorosulfonic acid, citric acid, cupric chloride, dry battery mixture, dye liquors (some), ferric chloride (as purchased), ferrous chloride, formic acid, hydrochloric acid, hypo (acid), iodine, lactic acid, mercuric chloride, oxalic acid, phosphoric acid, quinine bisulfate, quinine sulfate, sodium sulfate, sulfur chloride and ammonia, sulfur dioxide at 400° C., sulfuric acid, sulfurous acid, tartaric acid liquor, trichloracetic acid.

DISCUSSION.

W. C. Moore[8]: To me one of the most valuable features of this paper is the appendix. Among the media which satisfactorily

[8] Research Chemist, U. S. Industrial Alcohol Co., Baltimore, Md.

resist stainless steel are included quite a number of colloidal substances. On page 304, Mr. Hatfield discusses the effect of colloids in the case of vinegar.

It appears that it is the organic colloid in the vinegar which is instrumental in rendering the steel passive. In the previous paper Dr. Friend lists sucrose 0.05 per cent solution as an emulsoid. It seems to me that this is rather stretching a point.

W. Blum[9]: I noticed the same point. I did not comment on it for the reason that Dr. Friend's table shows definitely that the sucrose had no effect, namely, that he got 98 per cent corrosion in one case and 101 per cent in the other in the presence of sucrose, so that the paper contains evidence that it is not an emulsoid.

R. J. McKay[10]: There is another point in Dr. Hatfield's useful paper which is of interest for general considerations, and that is the effect of oxidizing agents as compared with acids in corrosion. He points out in the discussion of mine waters, for instance, that the stainless steels are very resistant to mine waters, provided the ratio of acid and ferric sulfate is correct. There has been published in this country by the Bureau of Mines much data on corrosion which would have been much more valuable if this fact had been taken into consideration. The action of an oxidizing agent, like ferric sulfate, is great in producing corrosion of nonferrous alloys. It is also active in preventing the corrosion of stainless steels and, therefore, in interpreting the results of the Bureau of Mines and the results of any corrosion tests on mine waters, we should take into full consideration the presence of ferric sulfate or other oxidizing agents. I have also found that ferric sulfate, as would be expected from the theory of the concentration cell, is very active in producing concentration cells.

B. D. Saklatwalla[11]: Why must you have the chromium between 12 and 14 per cent to make the so-called "stainless steel" stainless? Also, why is it that in the hardened condition it is stainless, and in the annealed condition it is absolutely not? There must be some fundamental reason for it. We are doing a lot of morphological work, but not enough histological work. We talk of protective colloids. If you have a non-corrosive material,

[9] Chemist, Bureau of Standards, Washington, D. C.
[10] Supt. Technical Service, International Nickel Co., New York City.
[11] Vanadium Corp., Bridgeville, Pa.

per se, why do you require protective coatings? I think that we ought to study a little bit more of the ultra-microscopic architecture of the ferrite grain. Sir Robert Hadfield has recently stirred up the question and again in a private communication to me, he writes: "Why is it that you have to have, say, about 12 per cent manganese in manganese steel, 12 per cent chromium in 'stainless steel,' and 12 per cent silicon in all these acid-proof irons?" He wanted to know if there was a virtue in the figure 12. As a matter of rather wide speculation, I might say that we have two forms of lattice cubes, the body centered and the face centered. The body centered cube has nine atoms and the face centered cube has 14 atoms. The numbers of atoms limit the practical range of 9 to 14 per cent. Now we know that in the ferrite lattice, when we introduce chromium as a solid solution, a substitution of the iron atoms takes place. Now that substitution probably is dependent on the relative number of atoms or on the relative masses that are present.

Another possibility is this: It may not be 9 per cent or 12 per per cent or 14 per cent of chromium that is effective; it may be a very high chromium content that imparts the resistance to corrosion. When the ferrite crystal grows, after solidification has started, it rejects any foreign matter, which in this particular case is chromium, as is a common characteristic of all cell or crystal growth. It pushes the chromium content ahead continuously during growth, so as to enrich the periphery of the grain, and you might thus have a ferrite grain which chemical analysis may show to contain 12 per cent or 14 per cent chromium; yet, you might have a highly concentrated chromium content surface layer on the ferrite grain, which may be responsible for the protection. The phenomenon of different corrosion resistance with heat treatment might also have something to do with this. In the annealed condition your chromium has a chance to migrate from the surface, and you get a weaker surface, that is, you permit the chromium to migrate into the body of the crystal, vitiating that film or protective layer.

Now, if study is directed along these lines to ascertain why the material itself is intrinsically resistant to chemical or electrochemical influences, I should consider this to be much more important. While I personally realize how extremely difficult it is

to carry out an investigation such as this experimentally, yet it is worth the effort, as it may throw some real light and we may then begin to know what corrosion actually it. All phenomena of corrosion are, undoubtedly, of electrolytic nature, but whether electrolysis is of prime importance, or whether there are more fundamental considerations that we are overlooking must yet be determined. In other words, a study of the fundamental qualities and qualifications of the ultra-microscopic ferrite grain, I think, is much more important than a study of merely the general relative conditions between micro-constituents. Of course, we are metallurgists and we must invite the physicist, the mathematician and the X-ray technician to assist in this matter.

Colin G. Fink[12]: I might add to what Dr. Saklatwalla said, that if we pushed the chromium not only outside the crystal, but pushed it clear to the surface of the alloy, we would not need any in the body of the metal. Thus you can make any steel non-corrosive by covering its surface with chromium or with a high chromium alloy.

G. M. Berry[13]: In line with what Dr. Saklatwalla has said (he is probably aware of it but possibly has overlooked it), among the patents which the American Stainless Steel Co. controls is one which covers chromium up to 60 per cent, and alloys are made, so-called "stainless steel" alloys, having chromium up in that range. This might tend to bear out the idea suggested, "pushing the chromium away from the iron into the surfaces," which become non-corrosive.

F. M. Becket[14]: In the abstract of Dr. Hatfield's paper it is stated: "The solubility in hydrochloric acid, and particularly in sulfuric acid, is increased in the case of the steels rich in chromium." Stainless steels in the 12 to 14 per cent chromium range are decidedly corrodible in sulfuric acid. However, if the chromium is increased to considerably higher percentages the alloys become decidedly resistant to sulfuric acid in practically all concentrations, hot and cold. I am sorry to say that I do not know the exact percentage of chromium corresponding to this much

[12] Head, Division of Electrochemistry, Columbia Univ., New York City.
[13] Chief Chemist, Halcomb Steel Co., Syracuse, N. Y.
[14] Vice-Pres., Electro Metallurgical Co., New York City.

greater resistance to sulfuric acid, because most of the work on this specific problem has been done in the range between 60 and 70 per cent chromium. Not a great deal of development work has been done along this line, for the simple reason that it has not been attractive commercially. These alloys are relatively expensive; with chromium contents of 60 to 70 per cent and decidedly low carbon content, these alloys could scarcely be classed as engineering materials. Nevertheless, it is a fact that if the chromium content is greatly increased, the alloys become very resistant to sulfuric acid. This, however, does not apply to hydrochloric acid.

It seems to me that in any range of chromium we cannot look upon these combinations of chromium and iron as simple alloys. All of us who have paid attention to this subject realize that the carbon content has a marked influence. For example, consider the two materials most prominent in the market, one of which is stainless steel. This alloy is supposed to require a hardening treatment—at least, if the maximum stainlessness is to be imparted. Now, if the chromium content of stainless steel is maintained, but the carbon content diminished from an original 0.30 or 0.40 per cent, to, say, below one-tenth of one per cent, the resulting alloy does not need the quenching or hardening treatment to make it stainless or non-rusting, as do the usual stainless steels. So, I believe we must correlate carbon with iron and chromium, just as in numerous other alloys we recognize the importance of the carbon content.

B. D. Saklatwalla: I think the point that Mr. Becket touched on, the carbon content, brings us back again to the same idea of the primary phenomena and the secondary phenomena. When you have carbon present only to such an extent as is absorbed in solid solution in the ferrite grain, your carbon becomes harmless. However, when you have a carbon content high enough so as to have it as a free constituent, in the form of say, pearlite, then probably your secondary phenomena begin to get so strong, your electrolytic action gets so pronounced, that the primary phenomena are masked by the secondary phenomena. In other words, it is not the percentage of carbon as a chemical constituent, but it is whether that carbon is there as free carbon or

not. If you can absorb the carbon, you are getting a more corrosion resistant steel at the same chromium content. That opens up another field—the addition of other elements into these alloys. If you introduce a third element which helps to keep the carbon in the absorbed and not in the free pearlitic condition, carbon becomes harmless and you do not require heat treatment to make the steel stainless. That is where all copper additions, silicon additions and a few others come in.

Colin G. Fink: In line with what Mr. Becket said, the resistance to corrosion increases with the chromium content, in particular the resistance to sulfuric acid. We must also remember that all this work of Dr. Hatfield's and others on stainless steel is applicable to room temperature only. As soon as we study the corrosion of the chromium steels at higher temperatures, we find that 12 to 16 per cent alloys no longer stand up. If we want steel to resist corrosion at, say, red heat, we will preferably go up to 30 per cent Cr, and if you go to still higher temperatures you must use 40 per cent Cr irons, and so on. Accordingly, Dr. Saklatwalla's magic number 12, or magic number 13, applies to room temperature only. At higher temperatures we must go up with the chromium content, and similarly we must go up with the silicon content in the ferrosilicons to make that alloy resistant to corrosion at higher temperatures. I am referring in particular to air corrosion.

B. D. Saklatwalla: I think, to supplement Dr. Fink's remarks, that those are two entirely separate phenomena, at ordinary temperature and at high temperature, because at high temperature there is no moisture. Not only that, but if we assume that in these chromium steels a protective film of oxide is formed, which seems to be the general consensus of opinion, the physical characteristics of that film at ordinary temperature and at red heat will be two entirely different things; its tenacity, its expansion, its ductility, and so on, will be different.

A paper presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 2, 1924, Dr. Saklatwalla in the Chair.

ELECTROLYTIC THEORY OF CORROSION.[1]

Comments on Wilder D. Bancroft's Recent Paper on Above Topic.

By F. N. Speller[2] and F. G. Harmon.[3]

Abstract.

It is shown that the electrolytic theory is the best theory of corrosion we possess today. Many cases of so-called pure "chemical corrosion" have not been correctly interpreted. Accelerated corrosion tests must be very carefully carried out, to avoid results that may be entirely different from results obtained by ordinary slow processes of corrosion. [C. G. F.]

In the lengthy article by Wilder D. Bancroft, of Cornell University, "The Electrolytic Theory of Corrosion,"[4] is to be found a vigorous and outspoken defense of the Electrochemical Theory as Bancroft himself sees it. The article, somewhat belated, has been called forth primarily as an answer to the "Sixth Report of the Corrosion Research Committee of the Institute of Metals," by Bengough and Stuart.[5] These authors have maintained that the function of oxygen in corrosion is usually one of direct chemical attack upon the metal, as opposed to an electrochemical attack, and in so doing they have assumed the electrochemical theory to be inadequate.[6] As a natural result they stand on the defense in a typical Bancroftian attack.

It is impossible in reviewing such a long article, made up almost entirely of quotations from various sources, to abstract the content, but brief mention of some of the major points can be made,

[1] Manuscript received Aug. 22, 1924.
[2] Metallurgical Engineer, National Tube Co., Pittsburgh, Pa.
[3] Metallurgist, Pittsburgh, Pa.
[4] J. Phys. Soc., **28**, 785-871 (1924).
[5] J. Inst. Metals, **28**, 88 (1922).
[6] Since publication of the sixth report Bengough has frankly accepted the electrochemical view. *Cf.* Journal Institute of Metals, **31**, 187 (1924).

and for a more complete study the reader would do well to consult the article itself. Bancroft's paper includes the most complete digest of the literature on the theory of corrosion that has yet been written, and should be of great value in future study of the subject.

He does well to point out that Bengough and Stuart, like some others who preceded them, were misled by the assumption that, according to the electrochemical theory of corrosion, a pure homogeneous metal would not corrode. Bancroft puts the factor of homogeneity in its right place when he says, "This unwarranted assumption (that the most homogeneous metal will corrode the least rapidly) has done a great deal to retard the effective study of corrosion, because attention has been concentrated unduly on the question of homogeneity, to the comparative exclusion of more important factors; and many people have believed that the electrolytic corrosion theory was justifiable only in case homogeneity was the most important factor in preventing corrosion."[7] Bancroft has presented a great deal of data to back up this statement.

Another point of considerable importance is his attempt to straighten out the present confusion between chemical and electrochemical action. Bengough and Stuart, after their original misconception on homogeneity, added another in defining as electrochemical all reactions which took place at an anode and cathode separated by definable distance, but as chemical those reactions where the anodic and cathodic reactions were not separated (anodes and cathodes were superimposed). Bancroft is right in assuming that these are one and the same thing, relative distance not entering into the principle at all. There is no reason why electrical transference of energy should be more difficult through infinitesimal distances than through appreciable ones. Bengough and Stuart have not changed the electrochemical theory by any arbitrary definition of direct chemical attack.

In connection with the development of the electrochemical theory it is pointed out that while Whitney realized that corrosion was of an electrolytic nature, and that hydrogen was formed by the corrosion reaction, yet it remained for Walker, in 1908, to designate the function of oxygen as a depolarizer. This gave rise to the present conception that hydrogen, deposited as the metal

[7] Parentheses by the authors.

enters solution, may escape either in molecular form or be oxidized to water by dissolved oxygen. Recent experiments in the National Tube Company's research laboratory have proved that hydrogen may be removed in both ways in corrosion in neutral water at 120 to 150° F. (49°-66° C.) although comparatively little is given off as gas.

Bancroft, as well as the rest of us, realizes the necessity of accelerated corrosion tests in corrosion investigations. He advises and even recommends the plausible fundamentals of an accelerated electrolytic test, but a careful consideration of the present knowledge of corrosion factors will indicate, beyond a doubt, such a procedure is premature at the present time.

Further investigations as to the relation which this test bears to corrosion in service should be made before it can be accepted as reliable, except for a very limited set of conditions. In accelerated tests all the factors must be present, and they should also bear about the same relation to one another as in service or very different results may be obtained. Two corrosion committees of the American Society for Testing Materials have undertaken a great amount of work on this problem, and have already made tentative recommendations regarding such tests.

The formation of hydrogen peroxide as an intermediate step in corrosion reactions, the fact that passivity of metals produced by solutions of the bichromates is probably not in opposition to the electrochemical theory, the importance of differential aeration, and the fallability of the ferroxyl test are points worth noting by those interested in the theoretical aspects of corrosion and have been well stressed by Bancroft.

In commenting on the development of corrosion theories, as outlined by Bancroft, it would seem that much of the confusion in the application of theories to corrosion has come from the investigator's one-sided view of the factors. This might have been avoided by listing all the known factors, and learning more as to the effect of each before attempting to establish a theory. In other words, a proper perspective of the known facts and factors involved would have seemed to be helpful, and would have prevented too much stress being laid on homogeneity, colloidal effects, film protection, the influence of oxygen concentration, dissimilar metals or dissimilar solutions in contact with the same metal, or

many other variables, the resultant of which, determined the rate of corrosion. We have found it convenient to divide all these factors into (1) primary factors, which affect the anodic or cathodic reactions, and (2) secondary factors (such as film protection), which do not enter into the fundamental corrosion reactions, but may be important in the course of time.

The experiments cited by Bancroft, recently made at Ithaca, which indicate that corrosion proceeds when the solution surrounding the cathode is agitated with hydrogen or nitrogen, but at a slower rate than when oxygen is used, due probably to frictional electrification, are significant.[8] In making corrosion tests in agitated solutions, this may have been a disturbing factor, which will account for some of the inconsistent results. In planning such tests in the future the rate and means of agitation and aeration should be clearly specified.

In commenting on the differential oxygen method of measuring corrosion, suggested by one of us, Bancroft erroneously refers to this as a long time test principally applicable to practical problems, when as a matter of fact it is the reverse and is of value mainly in investigating the initial tendency to corrosion under varying conditions of temperature, velocity and composition of metal and solutions.[9]

Our knowledge of corrosion has been built up by much painstaking work on the part of those investigators cited in Bancroft's article and many others. One advantage of an inventory of this kind is that it brings to light how little we know on certain points. Investigators might now do well to direct their attention on an experimental study of the factors involved in corrosion, so as to fill up the gaps in our knowledge of this problem, and later on return to see how these facts fit the theory. Such a study, based on the establishment of all the facts, would save the great amount of effort which has been lost in the past due to the assumption of theories and conceptions based on secondary phenomena and, as a result, sooner or later disproved and discarded. In the develop-

[8] Evans in the J. Inst. of Metals, 30, 239-82 (1923) has given a very plausible explanation of this phenomenon based on experimental study.

[9] Unfortunately Bancroft's article is not arranged conveniently for ready reference. Its permanent value would be greatly enhanced by a more logical arrangement, so that the long quotations may be identified throughout and the development of the subject matter more clearly indicated. A full index is almost essential to a work of reference of this kind.

ment of a theory, it is necessary to include the whole field of experience and preclude the overemphasis of any one factor. In doing so it is well to consider the mistakes of the past, as pointed out by Bancroft, and first try to broaden and adapt the present theory, which has so well stood the test of time, rather than discard it without trial or disproof for something new.

DISCUSSION.

F. N. Speller: I would like to add a word on chromium steels. I had an opportunity of investigating the manufacture of chrome irons, that is, ferro-chrome alloys with less than 0.08 per cent carbon. So far as the results have gone, the influence of chromium in water corrosion of iron is less marked in those alloys that are practically free from carbon than in the higher carbon chrome alloys, where heat treatment is an important factor. As a matter of fact, you must have over 11 per cent chromium to get slow corroding iron. Under water, *if the iron is not highly polished,* the difference in the rate of corrosion between ordinary open-hearth steel and these chrome-iron alloys is in the neighborhood of about 10 to 1. So they are not by any means non-corrodible, unless highly polished and heat treated.

W. G. Whitman[10] and R. P. Russell[10] (*Communicated*): Prof. Bancroft's personally-conducted tour of the literature on corrosion theory with its lengthy quotations shows in a very interesting manner the development of the electrochemical theory. His argument for the electrochemical theory could possibly have been made more effective by references to a number of papers which were published considerably in advance of Dr. Bancroft's contribution.

For example, the apparently abnormal behavior of copper has been convincingly explained by Evans. Bengough and Stuart, the proponents of the direct oxidation concept, have accepted Evans' explanation and have expressed[11] their belief in the electrochemical theory. Dr. Bancroft's attack of Bengough and Stuart, therefore, loses a certain amount of its force. It is also interesting to note

[10] Mass. Inst. of Technology, Cambridge, Mass.
[11] World Power, 1, 21 (1924).

that in spite of references to the impossibility of hydrogen gas evolution from iron submerged in water at ordinary temperatures, Shipley[12] has definitely shown that the evolution takes place in the absence of air even at a pH of 9. The work of Speller[13] and others on the formation of protective films in alkalies has received no mention.

In attempting to give a clear summary of the situation based almost exclusively on quotations, Dr. Bancroft undertook a practically impossible task.

[12] Can. Chem. and Met., 8, 121 (1924).
[13] Ind. Eng. Chem., 16, 393 (1924).

A paper presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 2, 1924, Dr. Saklatwalla in the Chair.

THE CORROSION OF IRON ALLOYS BY COPPER SULFATE SOLUTION.[1]

By C. M. Kurtz and R. J. Zaumeyer.[2]

Abstract.

Samples of 400 different forgeable iron alloys were subjected to the copper sulfate test. Those alloys containing chromium appeared the most resistant. Silicon was also found to be very effective. With certain alloys corrosion resistance was greater after heating the samples to redness and quenching in water. Tests at 93° C. were practically the same as those at room temperature. [C. G. F.]

Introduction.

By Oliver P. Watts.

A number of years ago, when a specimen of duriron first came into the hands of the writer, one of the first tests of its resistance to corrosion was to see if a bright and adherent electroplate could be obtained on it from an acidified solution of copper sulfate. Although iron and steel are so vigorously attacked by this solution that a good electroplate is not obtainable, the duriron sample was as readily plated as if it had been brass or copper. A few years later when stainless steel came on the market the writer found this also to be unattacked by a solution of copper sulfate. This simple test thus served to differentiate these two materials of known resistance to corrosion from the long list of alloy steels.

It was therefore thought that the application of this test to a large number of iron alloys might serve to divide the alloying elements into two groups, those which confer distinct resistance

[1] Manuscript received July 2, 1924.

[2] Dept. of Chem. Engineering, Univ. of Wisconsin, Madison, Wis.

to corrosion, and those which are unpromising, and may be rejected when attempting to render iron resistant by alloying. Such tests were carried out by two seniors in the chemical engineering department of the University of Wisconsin three years ago, but the results were not published at the time, because of the hope that a series of corrosion tests of the same alloys in acids could be carried out. As there is no prospect that this can be done in the immediate future, their report is now presented as a possible aid to those who are experimenting to render iron and steel resistant to corrosion by alloying.

A striking feature of the tests was the effect of even the smallest speck of fire-scale (black oxide) on the surface or in crevices, which invariably served as a starting point for the deposition of copper. This indicates the reason for the insistence by manufacturers of stainless steel upon a perfect surface, free from flaws. Another salient fact is the superiority of chromium over all other alloying elements, so far as used in these alloys. Invar, an iron alloy containing 36 per cent of nickel, is reported to be resistant to rusting and corrosion, yet the writer has spent much time during the past year in the attempt to find some element that can be added to invar and prevent its destruction by corrosion in a certain commercial use, without impairing its unique temperature coefficient of expansion. The copper sulfate test, which requires over 45 per cent of nickel alloyed with iron for effective resistance, proves to be a more reliable guide in this case than the published and supposed-to-be authoritative statements about invar.

While some of the authors' conclusions rest on a narrow foundation, and may be disproved by later and more extensive experiments, the data which they present are of permanent value. It should be noted that these tests were applied only to forgeable alloys of iron.

There are several methods in use at the present time for testing the corrodibility of alloys. The commonest one is the sulfuric acid test, which consists in immersing the specimen in the acid for several hours and determining the loss in weight. Another test is the salt spray test. In this, the specimen is enclosed for a number of days in a small box in which the atmosphere is kept satu-

rated with a solution of sodium chloride. As in the acid test, the loss in weight serves as an indication of the corrodibility. The third method, the one which was employed in this series of tests, is the immersion of the specimen in the solution of copper sulfate. It is a well-known fact that iron and some of its alloys, when immersed in a solution of copper sulfate, will cause copper to deposit on the surface of the metal. On the other hand, it has been found that certain other alloys, such as duriron and stainless steel, which are unusually resistant to corrosion, do not deposit copper from a sulfate solution. The application of this test to many different alloys should afford a means of determining the combinations and proportions of different elements which are likely to yield corrosion-resisting materials. This test has one decided advantage over those mentioned above, in that it gives almost immediate results.

During the course of the investigation, nearly four hundred alloys prepared from electrolytic iron were subjected to the copper sulfate test. These alloys had been made up a number of years before, in an investigation financed by the Carnegie Institution, for the purpose of obtaining data concerning certain physical properties. Most of the specimens were forgings which had been made from such small ingots that a considerable amount of scale had become included in the metal at the time of forging. A small portion of each specimen was ground free from scale, and a drop of copper sulfate placed on a part of the clean surface. The solution used was exactly normal in copper sulfate and about 0.07 *N* in sulfuric acid. Those specimens on which copper deposited readily were discarded, and those on which no copper deposited were set aside for further treatment. Those on which copper deposited slowly, and which were apparently on the border line, were saved for special heat treatment.

Of all the alloys tested, those containing chromium appeared to be the most resistant. When chromium was the only added constituent, at least 10 per cent was required to resist the action of copper sulfate. Silicon was also found to be very effective. Nickel is effective provided there is 6 per cent or more chromium present. Ten per cent nickel made a 7 per cent chromium alloy resistant. In another case, 14 per cent nickel was found to be effective with a 6 per cent chromium and 1.5 per cent silicon. This would indicate that if there is 6 per cent chromium present,

TABLE I.

Action of Copper Sulfate on Alloys Containing Chromium.

Composition (Per Cent)				Other Elements (Per Cent)	Action		
No.	Cr	Si	Ni		I	II	III
133H	0.5	0.5	..	.....	D	..	..
133I	1	0.5	..	.....	D	..	..
137A	1	...	..	.....	D	..	..
133A	2	0.6	..	.....	D	..	..
137B	2	...	..	.....	D	..	..
144Z	2	...	10	.....	D	..	..
150B	2	...	..	10 W, 10 Mo, 0.5 V, 0.40 C	D	D	..
155U	2	...	..	10 W	D	..	..
133J	3	0.5	..	.....	D	..	..
133D	3	0.8	..	.....	D	..	..
156F	3	...	8	.....	D	..	..
133E	4	1.1	..	.....	D	..	..
137C	4	...	..	.....	D	..	..
136M	5	1.0	..	4 Mo, 3 Mn	D	D	..
133B	5	1.4	..	.....	D	..	..
133X	5	1.5	..	12 Mn	D	..	..
136O	5	1.5	..	4 Mo, 12 Mn	D	D	..
160J	5	...	..	0.3 V	D	..	..
160H	5	...	..	0.5 V	D	..	..
160K	5	...	..	1. V	D	..	..
163A	5	...	..	2 W, 0.60C	D	D	..
163G	5	...	..	5 W, 0.60 C	D	..	..
154E	5	...	10	.....	D	D	..
133K	6	0.4	..	.....	D	..	..
133L	6	0.4	..	.....	D	..	..
136A	6	1.5	14	.....	ND	..	ND
147Z	6	1.3	..	.....	D	D	..
133F	6	1.7	..	.....	D	D	..
133T	6	4	..	.....	D	D	..
136D	6	...	..	.....	D	..	..
148A	6	...	..	18 W, 0.3 V, 0.40 C	ND	..	D
154F	7	...	10	.....	ND	..	ND
163B	7	...	..	3 W, 2 Mo	D	ND	..
126B	7.2	3	..	9 W	ND	..	ND
137E	8	...	..	.....	D	D	..
133M	8	1	..	.....	D	ND	..
136R	8	1	20	.....	ND	..	ND
133C	8	2.3	..	.....	D	ND	..
133Q	8	4.5	..	? C	D	D	..
121C	9.7	1.9	..	0.31 C	ND	..	..
144U	10	...	..	.....	ND	..	ND
146H	10	...	..	.....	ND	..	..
154H	10	1	10	.....	ND	..	ND
1-30-20	10	1.5	..	10 W, 5 Mo	ND	..	..
111S	10	2	..	.....	ND	..	ND
155K	10	2	..	0.3 V, 0.60 C	D dep slowly	D dep slowly	D-slowly

TABLE I—*Continued*

Action of Copper Sulfate on Alloys Containing Chromium.

Composition (Per Cent)				Other Elements (Per Cent)	Action		
No.	Cr	Si	Ni		I	II	III
137L	10	2	..	2 Ti	ND	..	..
146L	10	2	20	.....	ND	..	ND
146Z	10	2	..	20 W	ND	..	..
156P	10	2	..	2 W, 2 Mo, 0.3 V	ND	..	ND
154I	10	2	10	.....	ND	..	ND
122E	10	3	..	.....	ND	..	ND
126A	10	3	..	5 W	ND	..	ND
113Q	10	4	..	.....	ND	..	ND
112A	10	5	..	.....	ND	..	ND
133R	10	6	..	.....	ND	..	ND
154A	10	...	8	.....	ND	..	ND
154B	10	...	12	.....	ND	..	ND
156H	10	...	..	2 W, 0.3 V, ? C	ND	..	Slow
156I	10	...	..	2 W, 0.3 V, 0.60 C	D	ND	D
156J	10	...	..	2 W, 0.3 V, 0.60 C	D	ND	..
155R	10	...	..	5 Mo	ND	..	ND
155V	10	...	..	10 W	ND	ND	ND
155S	10	...	..	10 Mo	ND	..	..
154K	10	...	10	1.0 C	D	D	D
155L	10	...	..	0.3 V, 0.65 C	D	ND	..
160I	10	...	..	0.3 V	ND	..	ND
160G	10	...	..	0.5 V	ND	..	ND
163O	10	...	..	1.0 V	ND	..	D
156G	10	...	..	2 W, 2 Mo, ? C	Spots	ND	..
141C	10.3	2	..	1.0 V, 0.30 C	ND	..	Spots
136G	13	...	..	.....	ND	..	..
133O	13	0.5	..	.....	ND	..	..
133N	13	1.8	..	.....	ND	..	ND
133G	13	3.6	..	.....	ND	..	ND
133U	13	5.5	..	.....	ND	..	ND
141E	15	2	..	.....	ND	..	ND
5-25-20C	15	1	1	0.3 Mn, 1.0 C	ND	..	..
137H	16.2	...	..	.....	ND	..	..
136H	17	...	1.5	.....	ND	..	ND
137S	20	1	10	0.3 V	ND	..	..
136L	20	1	..	3 Mn	ND	..	ND
141G	21.4	1	..	1.0 V, 3 Mn	ND	..	..
141B	21.8	...	..	.....	ND	..	ND
136U	30	...	..	.....	ND	..	ND

the addition of 3 to 4 per cent of nickel is equivalent to 1 per cent chromium. Tungsten, added to 6 per cent chromium, is also effective. Eighteen per cent tungsten, together with 6 per cent chromium, produced an alloy which was apparently on the border line, showing that 4.5 per cent of tungsten is equivalent to 1 per

cent of chromium. This is further supported by the fact that 9 per cent tungsten added to an alloy containing 7.2 per cent chromium and 3 per cent silicon made it resistant, whereas it would have deposited copper without the tungsten. Molybdenum was found to have practically no effect when the chromium content was below 10 per cent, but the addition of 5 to 10 per cent of molybdenum to a 10 per cent chromium alloy greatly improved its resistance to the action of copper sulfate. The presence of carbon had a decided effect upon the corrodibility. Up to 0.31 per cent it was found to be harmless, but larger amounts caused copper to deposit. Small amounts of vanadium, 0.3 to 1 per cent, seemed to have no effect whatever.

A number of specimens which appeared to be on the border line, and also a few containing from 0.4 to 1 per cent carbon, were heated to a bright red heat for twenty minutes in a gas muffle and then quenched in cold water. As a result, a large percentage of those which had deposited copper in the first test were rendered resistant to the action of the sulfate solution. All of the 10 per cent chromium alloys containing up to 0.65 per cent carbon, which had at first been acted upon by the sulfate, resisted its action after the heat treatment. An alloy containing 8 per cent chromium and only 1 per cent silicon, which had deposited copper in the first test, was made resistant. This treatment was also found to improve the protecting action of tungsten and molybdenum, for a 7 per cent chromium alloy containing 3 per cent tungsten and 2 per cent molybdenum was effectively cured by quenching.

To test the effect of annealing, most of the specimens which had resisted the action of the copper sulfate in the first test, were heated to a bright red heat in a gas muffle for about half an hour, and allowed to cool slowly with the furnace. The subsequent test showed that those which, by their composition, were near the border line, had been rendered slightly less resistant. In three such cases there was from 0.3 to 1 per cent vanadium present. Those alloys containing from 0.4 to 0.65 per cent carbon, which had been previously quenched, were found to have lost their resistant qualities after annealing. The results of these three tests are given in Table I. The column headed I shows the results of the test on the specimens as received. Column II shows

Table II.

Alloys on which Copper Deposited.

No. of Specimens	Composition			
	Per Cent		Per Cent	
40	Cu	0.4 to 10		
2	V	0.3 to 0.4		
65	Ni	0.25 to 45		
6	Co	0.5 to 6		
8	Sn	1.0 to 10		
15	As	0.25 to 10		
9	Ag	1.0 to 10		
2	Pb	3.0		
6	Mo	5.0 to 16		
8	Bi	1.0 to 10		
7	Mn	0.25 to 10		
3	Se	0.25 to 1.3		
2	Al	2.3 to 2.5		
13	W	2.0 to 20		
22	Si	0.25 to 7		
10	Monel	2.0 to 20		
14	Cu	0.5 to 20	and Si	0.25 to 6.7
12	Mn	5.0 to 15	and Cu	0.5 to 3
14	Cu	1.0 to 10	and Al	0.5 to 4
2	Sn	1.5 to 3	and Si	1.0 to 4
2	Sn	2.0 to 4	and Al	1.0
3	Mo	2.0 to 10	and Mn	1.0 to 2
6	Mo	4.0 to 16	and V	0.5 to 1
5	Ni	2.0 to 6	and Cu	0.7 to 2
3	Ni	5.0 to 10	and V	0.5 to 3
3	Cu	3.0 to 5	and As	1.0 to 4
5	W	4.0 to 7	and V	0.3 to 0.4
4	Mo	5.0 to 10	and Ni	10 to 20
1	Mo	5.0	and W	5
4	Ni	0.5 to 15	and W	3 to 5
1	Mo	10.0	and Si	4
1	Sn	3.0	and Cu	1
			+ Al	1
1	Ni	3.0	and Mo	7.7
			+ Si	2

Table III.

Effect of Copper Sulfate on Alloys of Fe and Ni.

No.	Per Cent Ni	Action
150U	45	Slow deposit
154T	50	No deposit
173W	90	No deposit
173X	95	No deposit

the results of quenching, and column III, of annealing. D means that copper deposited, and ND means no deposit.

After the above experiments had been practically completed, a letter was received from a well-known steel company which specializes in corrosion-resistant alloys, in which they stated that, according to their experience, the copper sulfate test was unreliable, as the results were likely to vary with small changes of temperature and the length of time of immersion. They stated that they had found specimens which were resistant to copper sulfate at 70° F. (21° C.) to deposit at a temperature only two degrees higher.

In order to check these statements, all the specimens which had been found to be resistant at room temperature, approximately 70° F. (21° C.) were heated to 100° F. (38° C.), but the results did not differ in the least from those of the first test. The specimens were then heated to 200° F. (93° C.) and tested a third time. However, the results in every case were identical with those of the first two tests.

In order to ascertain the effect of time, all the specimens from the temperature test were ground free from scale for a distance of two inches from the end, and immersed in copper sulfate solution in such a way that only the clean surface came in contact with the solution. They were allowed to stand for five days, observations being taken at frequent intervals. Many of the specimens did not deposit copper at all, and on those which did, the deposit started, in every case, from microscopic cracks or scale inclusions, and spread from these points.

Had it been possible to obtain specimens which were perfectly free from imperfections, it is probable that there would have been no deposit whatever. The time test brought out one or two points of interest, which would otherwise have been passed by unnoticed. Two alloys, one containing 10 per cent chromium and the other containing 10 per cent chromium and 5 per cent molybdenum, were acted upon to an equal degree, while the alloy containing 10 per cent chromium and 10 per cent molybdenum was not attacked at all, showing that unless molybdenum is present in amounts greater than 5 per cent, it has practically no effect. In several cases the alloy was somewhat corroded at the end of the fifth day, and a black coating had formed, although the characteristic red

color of copper was lacking. Judging by these results, then, it would appear that time and temperature are not important factors in the copper sulfate test.

CONCLUSIONS.

1. When only chromium is alloyed with electrolytic iron, it must form at least 10 per cent of the alloy in order to make it resistant to the action of copper sulfate.

2. A 6 per cent chromium alloy may be made resistant by: (a) addition of 18 per cent tungsten; (b) addition of 14 per cent nickel. With 6 per cent chromium present, 4.5 per cent tungsten or 3 to 4 per cent nickel is equivalent to 1 per cent chromium.

3. A 7 per cent chromium alloy can be made resistant by: (a) addition of 10 per cent nickel, or 3.5 per cent nickel is equivalent to 1 per cent chromium; (b) by addition of 3 per cent silicon and 9 per cent tungsten; (c) addition of 3 per cent tungsten, and 2 per cent molybdenum, heating to bright red heat for twenty minutes and quenching in cold water.

4. An 8 per cent chromium alloy can be made resistant by: (a) addition of 1 per cent silicon and heat treatment as described above; (b) addition of 14 per cent nickel.

5. A 10 per cent chromium alloy is not affected by amounts of carbon less than 0.31 per cent, but from 0.4 to 0.65 per cent carbon causes copper to deposit. This can be prevented by heat treatment. One per cent carbon causes a deposit which cannot be prevented by heat treatment, even when 10 per cent nickel is present. Alloys containing carbon, which were resistant after quenching, became non-resistant after annealing. With 15 per cent chromium, 1 per cent carbon does not cause a deposit.

6. If a resistant alloy is near the border line with respect to chromium and silicon content, 1 per cent vanadium will cause a deposit after annealing.

7. If only nickel is alloyed with electrolytic iron, it does not begin to resist corrosion until the nickel content reaches at least 45 per cent.

8. The temperature at which the specimen is tested seems to have no effect.

9. The length of time of immersion seems to have no decided effect beyond that expected, of increasing the amount of deposit and rendering it darker in color.

10. Five per cent molybdenum added to a 10 per cent chromium alloy apparently has no effect, although 10 per cent molybdenum has a protecting action.

11. Manganese seems to have no effect whatever.

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DISCUSSION.

H. S. Rawdon[3]: We have made use of this test at the Bureau of Standards recently. We collected specimens of all the various types of commercial stainless and rustless steels that manufacturers would give us. We wanted to test these to supplement a series of investigations we had on the straight chromium carbon steels that have been in use during the last few years. We found this test that Dr. Watts has described a useful one for grading these steels we had received, and later we hope to be able to show whether the results we get from the copper sulfate immersion test in any way check up with the results we get from our other tests, and with the real service that one can expect from those alloys.

R. J. McKay[4]: It is probably true that this test is a useful one. However, it seems to me that it is hard to assume that the resistance of a metal to atmospheric corrosion will really parallel its resistance to copper sulfate solution. The conditions are very different, and I do not see that the corrosion by copper sulfate is much closer to atmospheric conditions than the corrosion by a weak aerated acid. Why would not a test in which you use a very weak acid with a sufficiently large amount of air, in order to obtain results in a short period of time, be closer than the copper sulfate test?

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[4] Supt. of Technical Service, International Nickel Co., New York.

O. P. WATTS[5]: An answer to Mr. McKay is given in the paper on Stainless Chromium Steels (p. 297). Corrosion of stainless and carbon steels in sulfuric and hydrochloric acids showed on the average only a slightly greater resistance by the stainless steels. If we accepted the acid test as a criterion of the resistance to atmospheric corrosion of stainless and carbon steels, we should conclude that the former would prove only slightly superior, while, if we judged by the copper sulfate test, we would place the two kinds of steel in absolutely different classes as regards resistance to atmospheric corrosion, which agrees with the facts.

R. J. MCKAY: Agreement with actual experience is the only real proof that a test is good or bad. If the test shows a definite parallelism with practical service, then it should be used.

COLIN G. FINK[6]: Corrosion being electrochemical and the test described by Professor Watts being electrochemical, therefore, we would expect the test to be a good one. If there is any relation at all, any indication that the copper sulfate test will show us which alloy will resist atmospheric corrosion, then there is a definite value in the copper sulfate test. There is no doubt, however, that as far as the practical user goes, he is not interested in anything like a "copper sulfate" test. He wants to know how did the metal or alloy stand up in actual service?

R. J. MCKAY: I concur heartily in Dr. Fink's remarks. On the other hand, I think we all, as electrochemists, ought to take into consideration that we are often in the position of demonstrating that the laboratory is producing useful work. In our company the value of corrosion work is one of the hardest things to demonstrate. There seems to be a general feeling among engineers and practical men that a laboratory corrosion test is useless for practical purposes. We have progressed to a point where we know enough about corrosion to say that certain laboratory tests are useful, and we should not weaken our position by attempting to use results which are open to doubt.

J. A. MATHEWS[7]: Commenting on what the last speaker said, I agree with him that the copper sulfate test is a good test to see

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[6] Head, Division Electrochemistry, Columbia University, New York.
[7] Vice-President, Crucible Steel Co. of America, New York City.

if copper sulfate will corrode a particular metal, but not to compare various alloys, nor to predict what their behavior will be toward other reagents. In practice we are often misled by the laboratory test. In Dr. Hatfield's paper (p. 297), he illustrated that point in several instances; he showed that lactic acid, for instance, of a given strength readily attacked some stainless steels, whereas the same steel successfully resisted corrosion in sour milk containing the same percentage of acid. The same is true of citric acid *versus* lemon juice. I think most of you are familiar with the test made on the non-corrosive properties of steels in mine waters by the Bureau of Mines. Rezistal was totally resistant, while monel metal in that case was badly attacked. If you take the same two alloys and put them in beakers of sulfuric acid, rezistal will be somewhat attacked, while the monel metal will be very slightly affected. It has been difficult, indeed, to translate our laboratory experience into terms of expectations of the probable behavior of materials in service, and we have to be very careful in submitting materials to a customer to decide what particular alloy is good for the purpose intended.

A paper presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 2, 1924, Dr. Saklatwalla in the Chair.

EFFECT OF REDUCED PRESSURE ON RATE OF CORROSION OF AMALGAMATED ZINC IN ACID AND IN ALKALI SOLUTIONS.[1]

By E. W. Greene and O. P. Watts.[2]

Abstract.

There is a definite acceleration of the corrosion of amalgamated zinc in sulfuric acid by a vacuum. This acceleration is effected either with or without air in the solution. There is a retardation of the corrosion of amalgamated zinc in sodium hydroxide by a vacuum. This retardation takes place with or without air in the solution, but is greatest with the air present. There is a retardation of the corrosion of lead in acetic acid by a vacuum. This retardation is effected with or without air in the initial solution, but is greatest with the air excluded.

Carhart,[3] in his book on "Primary Batteries," makes this statement: "When amalgamated zinc is plunged in water, acidified with one-twentieth of its volume of sulfuric acid, it is not attacked at ordinary atmospheric pressure. But if a vacuum is produced above the liquid, bubbles of hydrogen are again freely evolved from the zinc surface. Upon readmission of air, bubbles again adhere to the plate, and the chemical action is arrested." He considered this as evidence that a vacuum accelerates corrosion by removing a film of polarizing hydrogen.

In investigating the corrosion of metals by acids, O. P. Watts and N. D. Whipple[4] questioned the statement of Carhart, and in order to disprove it they tested the relative corrosion of several metals under a vacuum and at atmospheric pressure. In every case they found that the effect of the vacuum was to retard corrosion. The results of these experiments are reproduced in

[1] Manuscript received July 2, 1924.
[2] University of Wisconsin, Madison, Wis.
[3] Primary Batteries, p. 34 (1891).
[4] Trans. Am. Electrochem. Soc., 32, 257 (1917).

Table I, as they directly bear on the subject in hand. In explaining their results these investigators attributed the retarding effect of the vacuum as being due to the removal of depolarizing air from the solution. They did not, however, test amalgamated zinc, about which Carhart had made his statement.

TABLE I.

Effect of Vacuum on Corrosion of Metals.

Temperature, 21 to 22° C.; Time, 45 hr.; Area, 60 sq. cm.

No.	Metal	Reagents Used	Loss in g.
		In vacuum, 2.4 to 3.5 cm. of mercury.	
107	Fe	N H_2SO_4 190 cc.	0.7332
108	Fe	N H_2SO_4 190 cc., 0.25 g. Na_3AsO_4	.0.0083
109	Pb	N CH_3COOH 190 cc.	0.0374
110	Cu	N H_2SO_4 190 cc.	0.0044
111	Zn	N NaOH 190 cc.	0.0101
		At Atmospheric Pressure.	
112	Fe	N H_2SO_4 190 cc.	1.6266
113	Fe	N H_2SO_4 190 cc., 0.25 g. Na_3AsO_4	0.0287
114	Pb	N CH_3COOH 190 cc.	0.0841
115	Cu	N H_2SO_4 190 cc.	0.0208
116	Zn	N NaOH 190 cc.	0.0772

In these investigations it was recognized that possibly both Carhart and the later experimenters were right, and that the vacuum might produce two opposite effects on the rate of corrosion: (1) Accelerate corrosion by partially removing the adhering film of polarizing hydrogen; (2) Retard corrosion by removing the depolarizing oxygen from the solution.

If oxygen was removed from the corroding solution by boiling, and was kept out by a layer of oil on the surface of the solution, the retarding effect of the vacuum would be eliminated, and the vacuum should accelerate corrosion by removing the hydrogen.

Accordingly, in the first set of data four specimens were put in boiled $2N$ H_2SO_4, and the surface of the acid was covered with 0.125 to 0.250 in. (3.18 to 6.35 mm.) of gas-engine lubricating oil. Two of these were put under the vacuum obtained from a laboratory filter pump, and two were left under atmospheric pressure. At the same time the total effect of the vacuum was investigated

by placing four specimens in unboiled acid with no oil on the surface, and putting two of these in the vacuum, and leaving two at atmospheric pressure. Amalgamated zinc was used, because this had not been used by recent investigators, and because it was referred to by Carhart. The result is shown in Table II.

TABLE II.

Corrosion of Amalgamated Zinc by 2N Sulfuric Acid.

Temp. 25° C., time 116 hr. Zinc slightly amalgamated electrolytically, area 7.5 sq. cm. Volume of acid 300 cc.

No.	Pressure	Treatment	Covering	Loss in g.
1	Atmosphere	None	None	0.3882
2	Atmosphere	None	None	0.3886
3	10 cm. Hg	None	None	0.3991
4	10 cm. Hg	None	None	0.3854
5	Atmosphere	Boiled	Oil	0.0545
6	Atmosphere	Boiled	Oil	0.0300
7	10 cm. Hg	Boiled	Oil	0.0678
8	10 cm. Hg	Boiled	Oil	0.0989

Specimens 1, 2, 3, 4 show a slight acceleration of corrosion under the vacuum, but within experimental error. It must be concluded that the vacuum either has no effect, or that the accelerating and retarding effects counterbalance each other.

In the case of the specimens where the air was removed by boiling (5, 6, 7, 8) the vacuum causes from 24 per cent to 230 per cent more corrosion. Therefore, it would seem that the effect of the vacuum on the hydrogen film was such as to increase the corrosion.

In the first test it was noticed that some of the specimens were corroding unevenly—bubbles of hydrogen gas were unevenly distributed over the surface. This may have been due to insufficient amalgamation. The second test was run on the same specimens amalgamated by rubbing the mercury in. In this second test two specimens were put in boiled acid with no oil on the surface, and put under the vacuum to determine the effect of the oil. See Table III.

A comparison of specimens 9 and 10 with 15 and 16 shows that even under the vacuum the effect of the oil in keeping out oxygen

and preventing its depolarizing action is great. Specimens 11 and 12 show that the resulting effect of the vacuum is to increase corrosion. It should be noted that the corrosion is greater under the vacuum, even in the case of the boiled specimens 9 and 10. The effect of the vacuum when the air is excluded from the solution by oil is uncertain, because specimens 13, 14, 15 and 16 lead to no conclusions. The large discrepancy between specimens 15 and 16 could not be accounted for, unless there was faulty amalgamation of 16.

TABLE III.

Corrosion of Amalgamated Zinc by 2N Sulfuric Acid.

Conditions as in Table II, except that the zinc was amalgamated by rubbing with mercury, and the time was 142 hr. and the vacuum only 18 cm. of mercury.

No.	Pressure	Treatment	Covering	Loss in g.
9	18 cm. Hg	Boiled	None	0.6988
10	18 cm. Hg	Boiled	None	0.6611
11	Atmosphere	None	None	0.5603
12	18 cm. Hg	None	None	0.7628
13	Atmosphere	Boiled	Oil	0.0118
14	Atmosphere	Boiled	Oil	0.0158
15	18 cm. Hg	Boiled	Oil	0.0094
16	18 cm. Hg	Boiled	Oil	0.0155

At this point it was decided to use a pure metal, such as lead, for the purpose of obtaining more uniform results, and to see if the results checked those obtained with the amalgamated zinc. Pure "test lead" in thin sheets was used. The object of the thin sheets was to increase the accuracy by increasing the proportion of surface to weight. As the effect of the vacuum with no air present was the principal result wanted, twelve specimens were put in boiled acid with oil. Four more were used in unboiled acid to determine the effect of the vacuum alone. The results are shown in Table IV.

The result of this test are exactly opposite to the experiments with amalgamated zinc, and as they are remarkably uniform they may be considered fairly reliable. Instead of increasing corrosion, as in specimens 5 and 6, the effect of the vacuum alone is about the same as boiling the solution and then excluding the air by oil, *viz.*, a reduction of corrosion to 35 per cent. The placing

TABLE IV.

Effect of Diminished Pressure on Corrosion of Lead by N Acetic Acid.

Temp. 16-29° C. Time 285 hr. Surface exposed 37 sq. cm. Volume of acid 300 cc.

No.	Pressure	Treatment	Covering	Loss in g.
17	Atmosphere	Boiled	Oil	0.1261
18	Atmosphere	Boiled	Oil	0.1061
19	Atmosphere	Boiled	Oil	0.1062
20	Atmosphere	Boiled	Oil	0.1040
21	Atmosphere	Boiled	Oil	0.1096
22	Atmosphere	Boiled	Oil	0.1058
23	10 cm. Hg	Boiled	Oil	0.0108
24	10 cm. Hg	Boiled	Oil	0.0124
25	10 cm. Hg	Boiled	Oil	0.0145
26	10 cm. Hg	Boiled	Oil	0.0145
27	10 cm. Hg	Boiled	Oil	0.0187
28	10 cm. Hg	Boiled	Oil	0.0165
29	Atmosphere	None	None	0.2734
30	Atmosphere	None	None	0.3285
31	10 cm. Hg	None	None	0.1175
32	10 cm. Hg	None	None	0.1017

TABLE V.

Effect of Diminished Pressure on Corrosion of Amalgamated Zinc in N Sodium Hydroxide.

Temp. 16-29° C. Time 285 hr. Surface exposed 15 sq. cm. Volume of solution 300 cc.

No.	Pressure	Treatment	Covering	Loss in g.
33	Atmosphere	Boiled	Oil	0.0200
34	Atmosphere	Boiled	Oil	0.0210
35	10 cm. Hg	Boiled	Oil	0.0080
36	10 cm. Hg	Boiled	Oil	0.0063
37	Atmosphere	None	None	0.0451
38	Atmosphere	None	None	0.0448
39	10 cm. Hg	None	None	0.0142
40	10 cm. Hg	None	None	0.0126

of this last solution under a vacuum reduces corrosion still further to only 4 per cent of its initial value.

In order to determine if this effect of a vacuum is confined to acids only, amalgamated zinc specimens were corroded in normal alkali. The results, which are recorded in Table V, do not agree

TABLE VI.

Effect of Time on Corrosion of Amalgamated Zinc in 2N Sulfuric Acid.

Time 107 hr. Temp. 18-24° C. Surface exposed 15 sq. cm.

No.	Pressure	Treatment	Covering	Loss in g.
41	Atmosphere	Boiled	None	0.0707
42	Atmosphere	Boiled	None	0.0812
43	Atmosphere	Boiled	None	0.1127
44	Atmosphere	Boiled	None	0.0851
45	10 cm. Hg	Boiled	None	0.1075
46	10 cm. Hg	Boiled	None	0.3066
47	10 cm. Hg	Boiled	None	0.1448
48	10 cm. Hg	Boiled	None	0.1147

TABLE VII.

Effect of Time on Corrosion of Amalgamated Zinc in 2N Sulfuric Acid.

Time 43 hr. Temp. 18-27° C. Other conditions as in Table VI.

No.	Pressure	Treatment	Covering	Loss in g.
49	Atmosphere	Boiled	None	0.0279
50	Atmosphere	Boiled	None	0.0316
51	Atmosphere	Boiled	None	0.0330
52	Atmosphere	Boiled	None	0.0294
53	11 cm. Hg	Boiled	None	0.0320
54	11 cm. Hg	Boiled	None	0.0373
55	11 cm. Hg	Boiled	None	0.0350
56	11 cm. Hg	Boiled	None	0.0367

with those obtained with amalgamated zinc in acid. With unboiled solutions the vacuum reduces corrosion 30 per cent, and is more effective than boiling and covering the solution with oil. The combined effect of boiling, covering with oil and subjecting to reduced pressure is to lower corrosion to only 1.6 per cent of the loss in the original solution.

Two other tests were run on the amalgamated zinc specimens in acid, boiled and with no oil on the surface, the object being to check the results shown by specimens 9, 10, 11 and 12, namely, that the corrosion of amalgamated zinc is accelerated by the vacuum. These results appear in Tables VI and VII, and verify

the results mentioned above. The test recorded in Table VII was run for a comparatively short time to see if cutting down the amount of corrosion would render the results more uniform.

The experiment recorded in Table VI (omitting specimen 46) shows 58 per cent more corrosion under the vacuum than at atmospheric pressure. The experiment recorded in Table VII shows 15 per cent more corrosion under vacuum. The rate of corrosion has evidently increased with time. This may be due either to increase of surface as the specimen becomes roughened by corrosion, or to diffusion of mercury from the surface into the zinc, which was 0.165 cm. (0.065 in.) thick, so that the concentration of the protective mercury on the surface became less, or to the combined effect of both of these actions.

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DISCUSSION.

COLIN G. FINK[5]: Prof. Watts emphasizes the very important point that corrosion measurements in solution, as published in the literature, often do not check at all, even though two authors use the same concentration of sodium chloride solution or the same concentration of acid. Due, say, to the fact that one solution was prepared hot and the other solution prepared cold, or one contained an over abundance of air while the other did not, you get entirely different corrosion results. This effect of air in solution is very pronounced in the dissolution of copper or tin in acids. In the case of the copper coulometer we must counteract the action of air by adding ethyl alcohol to the solution. The effect of air is often so insignificant that ordinarily it is overlooked; yet, when we compare the results of one author with those of another, we can not check them, due in many cases to the mere difference in the method of preparing the solutions.

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A paper presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 2, 1924, Dr. Saklatwalla in the Chair.

TESTS FOR GRADING CORROSION-RESISTING ALLOYS.[1]

By Wm. E. Erickson and L. A. Kirst.[2]

Abstract.

As a rapid method of selecting from a large number of iron alloys those which would possess the rust-resisting qualities of stainless steel, Kurtz and Zaumeyer[3] applied an acidified solution of copper sulfate to the cleaned metal surface. While this test probably detected all alloys having marked resistance to corrosion, it did not differentiate between those of high and those of only moderate resistance. The experiments, results of which are here reported, were undertaken in the hope of separating these alloys into several groups according to their resistance to corrosion. The alloys were tested with solutions of $CuSO_4$, $AgNO_3$, $PtCl_4$, $AuCl_3$ and $PdCl_4$. Of the common metals silicon and chromium appear to be the most resistant to corrosion. The addition of either or both of these elements to iron reduces the corrodibility very appreciably.

THEORY OF PROPOSED TEST.

The theory used as a working hypothesis in the method to be proposed, is as follows:

1. Every metal or alloy has what is termed a solution pressure, or a measurable tendency to go into solution. The magnitude of this varies for each different material. It is, therefore, possible to arrange them in a series so that those metals which have the higher solution pressures are near the top. Such a series has already been established, and is known as the electrochemical series. As an illustration of the workings of this arrangement we might take as an example zinc and gold in a chloride solution, in which the former has a higher solution pressure. A drop of

[1] Manuscript received July 2, 1924.
[2] University of Wisconsin, Madison, Wis. Senior thesis, 1921.
[3] Kurtz and Zaumeyer. This volume, p. 319.

gold chloride solution is placed upon metallic zinc. The zinc, having a higher solution pressure, displaces the gold in the solution until the gold is almost all plated out. From this it is concluded that a metal of high solution pressure will precipitate a metal of low solution pressure.

2. From the foregoing it is seen that the lower a metal is in the series, the greater is its resistance to being dissolved; and, consequently, the greater is the resistance to corrosive agents, atmospheric and otherwise. This simply brings us back to the method used to formulate the original electrochemical series. In this method, solutions of salts of the various metals were made, and strips of each metal were then dipped into each solution. In some cases the metal in solution plated out and metal from the strip went into solution, while in others nothing occurred. A table was then arranged, in which any metal displaced or plated out any metal lower in the series. In other words, each metal in such a series is more resistant to corrosion than those above it in the series. We considered using a method similar to the above to grade corrosion-resisting alloys. By means of the electrochemical series, a series of solutions can be prepared, each more corrosive than the previous one. By testing any specimen with a drop or two of each of these solutions in order of their increasing corrosiveness, some solution will be found from which the metal will plate out. The same will hold true of each succeeding solution. By this means we should be able to differentiate between the resistances to corrosion of the various metals and alloys, and to separate these into groups.

The advantages claimed for this particular method are that it can be performed in a much shorter period of time, and is nearly as conclusive as an acid test. Even with the most resistant alloys, results can be obtained in less than five minutes.

According to the meager data obtainable in text books, palladium is placed between platinum and silver in the electrochemical series. However, in all of our experiments a palladium chloride solution was found to be more corrosive than the chloride solutions of either gold or platinum. Since we had regarded the solution pressure of palladium as between that of silver and platinum, we made new potential measurements to determine its

TABLE I.

Results of Tests on Pure Metals.

X indicates the deposition of the metal in solution.

	$CuSO_4$	$AgNO_3$	$PtCl_4$	$AuCl_3$	$PdCl_4$
Silicon	0	0	0	0	0
Chromium	0	0	0	0	0
Tungsten	0	0	0	0	X
Nickel	0	0	X	X	X
Molybdenum	..	X	X	X	X
Manganese	X	X	X	X	X

TABLE II.

Results of Tests on Non-Ferrous Alloys.

X indicates the deposition of the metal in solution.

Cr Per Cent	Si Per Cent	Ni Per Cent	W Per Cent	Monel* Per Cent	Other Metals Per Cent	$CuSO_4$	$AgNO_3$	$PtCl_2$	$AuCl_3$	$PdCl_2$
20	..	40	40	..	.....	0	0	0	X	X
10	2	63	15	..	10 Mo	0	0	0	X	X
..	..	50	50	..	.....	0	0	0	X	X
20	2	78	..	..	.....	0	0	X	X	X
10	..	..	15	75	.....	0	0	X	X	X
10	2	..	..	88	.....	0	0	X	X	X
10	2	..	15	..	73 Fe, 10 Mo	0	0	X	X	X
10	1	..	..	..	64 Fe	0	0	X	X	X
13	2	..	..	..	0.1 C	0	0	X	X	X
13	1.3	..	..	..	0.4 C	0	0	X	X	X
†	..	..	5	75	.....	0	0	X	X	X
20	2.5	..	15	77.5	.....	0	X	X	X	X
12	2	..	..	81	.....	0	X	X	X	X
15	..	..	..	60	10 Mo	0	X	X	X	X
10	..	..	..	90	.....	0	X	X	X	X
20	1.5	..	..	78.5	.....	0	X	X	X	X

* These alloys were made by adding different elements to the indicated quantity of monel metal.

† Fe-Cr 25 per cent.

position. A potentiometer was used to measure the difference of potential between the palladium and a normal calomel electrode in a normal potassium chloride solution with the following results:

Palladium (plated)	Gold	Platinum
—0.78	—0.55	—0.53

TABLE III.

Tests of Ferrous Alloys.

No.	Cr Per Cent	Si Per Cent	Ni Per Cent	V Per Cent	Other Metals Per Cent	$CuSO_4$	$AgNO_3$	$PtCl_4$	$AuCl_3$	$PdCl_4$
126A	10	3	..	..	5 W.....	0	0	X	X	X
126B	7.2	3	9	..	.....	0	0	X	X	X
133N	13	1.8	..	..	.....	0	0	X	X	X
133R	10	6	..	..	.....	0	0	X	X	X
133V	13	5.5	..	..	.....	0	0	X	X	X
133O	13	0.5	..	..	.....	0	0	X	X	X
133G	13	3.6	..	..	.....	0	0	X	X	X
133C	8	2.2	..	..	.....	0	0	X	X	X
136L	20	1	..	..	3 Mn.....	0	0	X	X	X
136U	30	1	..	..	3 Mn.....	0	0	X	X	X
136H	17	1.5	..	..	.....	0	0	X	X	X
136G	13	..	..	..	.....	0	0	X	X	X
136R	8	1	20	..	.....	0	0	X	X	X
137S	20	1	10	..	0.3 Mn.....	0	0	X	X	X
137B	2	..	..	..	.....	X	X	X	X	X
137H	16.2	..	..	..	.....	0	0	X	X	X
137L	10	2	..	..	2 Ti.....	0	0	X	X	X
141B	21.8	..	..	..	.....	0	0	X	X	X
141G	21.4	1	..	1	3 Mn.....	0	0	X	X	X
141C	10.3	2	..	1	.....	0	0	X	X	X
144U	10	..	..	..	.....	0	0	X	X	X
146H	10	..	..	..	.....	0	0	X	X	X
146L	10	2	20	..	.....	0	0	X	X	X
148A	6	..	..	0.3	18 W; 0.4 C.	0	0	X	X	X
154G	10	..	10	..	.....	0	0	X	X	X
154B	10	..	12	..	.....	0	0	X	X	X
154I	10	2	10	..	.....	0	0	X	X	X
154K	10	..	10	..	1 C.....	0	0	X	X	X
154A	10	..	8	..	.....	0	0	X	X	X
111S	10	2	..	..	.....	0	0	X	X	X
122E	10	3	..	..	.....	0	0	X	X	X
133M	8	1	..	..	.....	0	0	X	X	X
136A	6	1.5	14	..	.....	0	X	X	X	X
154F	7	..	10	..	.....	0	0	X	X	X
155L	10	..	..	0.3	0.65 C.....	0	0	X	X	X
155K	10	2	..	0.3	0.6 C.....	0	0	X	X	X
113N	..	3.7	..	..	.....	0	0	X	X	X
155R	10	..	..	..	10 Mo.....	0	0	X	X	X
155S	10	..	..	..	5 Mo.....	0	0	X	X	X
155V	10	..	..	..	10 W.....	0	0	X	X	X
156G	10	..	..	0.2	2 W.....	0	0	X	X	X
156H	10	..	..	0.3	2 W.....	0	0	X	X	X
156I	10	..	..	0.3	2 W; 0.6 C.	0	0	X	X	X
156J	10	..	..	..	2 W; 0.6 C.	0	0	X	X	X
156P	10	2	..	0.3	2 W.....	0	0	X	X	X

Although these measurements may be subject to error, they bear out the results obtained in our work with palladium chloride

as a corrosive agent. In every case where an alloy was used, the palladium plated out of solution, whereas in several different instances where high tungsten, chromium, and silicon alloys were tested, the platinum chloride solution was non-corrosive to the extent of deposition.

On the basis of these facts and assumptions, five solutions were made up, each more corrosive than the preceding. The solutions, in order of their corrosive power, and the position of the metal in the electrochemical series, are as follows:

Copper Sulfate
Silver Nitrate
Platinum Chloride
Gold Chloride
Palladium Chloride

The test was applied to the metals and alloys listed by grinding a spot free from scale, polishing with tripoli on standard polishing wheels, removing polishing grease in the electric cleaner, and applying a drop of the corrosive solution. According to our views, if copper sulfate deposited copper on a strip of metal, each succeeding solution ought to deposit its metal out of solution. In every case this assumption held true. Again, if gold chloride does not precipitate gold on the metal, it is expected that none of the previous solutions will deposit their metal on the specimen. This also held true without exception.

The results of these tests are shown in the accompanying tables. The data in Table I show the results of tests on the pure metals, which we supposed were quite resistant to corrosion. Table II deals with non-ferrous alloys, and Table III concerns our findings on ferrous alloys.

CONCLUSION.

The data from the tests on alloys of chromium, silicon and tungsten show that these alloys are quite resistant to corrosion. This statement is generally considered true, as it has been known by others for some time. However, this fact is borne out more conclusively by the observed resistances to corrosion of the pure metals. Silicon and chromium resisted corrosion even by palladium chloride, while tungsten was affected only by this solution. Generally speaking, chromium and silicon seem to be the two

metals most resistant to corrosion, and their presence in an alloy in a reasonable percentage would seem to be desirable to prevent the action of corrosive agencies.

When over eight per cent of chromium is present in an iron alloy, the amount is sufficient to prevent the deposition of silver. The deposition of platinum, gold and palladium is not prevented by making the chromium content even as high as 30 per cent. Hence, any additional chromium does not give an advantage commensurate with the increase in cost due to the chromium. In one specimen where the only alloying metal present is 4 per cent of silicon, the same degree of protection is afforded as is given by 8 or 10 per cent of chromium. It appears to be true that when the silicon and chromium are present in amounts sufficient to prevent corrosion to a markedly increased degree, there is formed a solid solution by the two metals.

This method of testing for corrosion appears to be promising. In no cases were the theories of the procedure reversed by the facts. The foregoing shows that the basis for our assumptions was sound.

Practically all of the ferrous alloys above 8 per cent chromium are located in the interval between silver nitrate and platinum chloride, because they allow the deposition of platinum and not that of silver. From the above there would seem to be a need for an intermediate testing reagent, which would serve to further differentiate between the corrosion-resisting properties of the different alloys. We, however, did not know of any metal whose solution pressure was intermediate between that of platinum and silver.

These experiments show that the method is rather promising. It furnishes a means of selecting from a large number of alloys those which are highly resistant to corrosion, and of separating these into groups according to their probable resistance to corrosion. The real merit of these tests can only be learned by testing a series of alloys which have been graded by these tests, under actual service conditions.

All alloys tested are much more expensive and resistant than are likely to be employed to resist atmospheric corrosion, and are such as might be used successfully in places where corrosion is

very severe, as in chemical manufacture. For selecting alloys for such uses the acid test should doubtless be applied in addition to the tests here employed.

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DISCUSSION.

O. P. WATTS[4] (*Communicated*): In applying this method of testing it should be noted that the acid-radical as well as the metal of the corroding solution is a factor in the result produced. Several metals and alloys owe their resistance to corrosion to a protective film of oxide on their surfaces, a film which is not capable of displacing metals from solution in the manner of this test, and which may, in certain cases, be dissolved by only a few of the long list of known corrosive solutions. This is brought out in the following data obtained by George P. Ryan.[5]

In a solution of copper sulfate none of the following caused the deposition of copper, but on adding a few drops of hydrofluoric acid copper plated out:

	Per Cent	Per Cent
Stainless steel	12 Cr	0.3 C
137L Iron	10 "	2 Si
133R Iron	10 "	6 Si
133O Iron	13 "	0.5 Si
133N Iron	13 "	1.8 Si
133G Iron	13 "	3.6 Si
133U Iron	13 "	5.5 Si
137H Iron	16.2 "	..
Iron	20 "	1.5 Ni
Silicon	..	..
Duriron	..	..

No deposit of copper appeared on the following even on addition of hydrofluoric acid:

Chromium.
Ferrochromium, 70 per cent Cr.
Molybdenum-chromium, 50 per cent Cr.

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[5] University of Wisconsin.

In the use of many non-corrosive alloys this harmful effect of some particular acid-radical is often encountered. The immunity of duriron to attack by sulfuric and nitric acids, and its corrosion by hydrochloric acid is a well-known example of this. By varying the acid-radical as well as the metal in the corroding solutions, it should be possible to differentiate between corrosion-resisting alloys even more completely than has been done in these tests.

B. D. SAKLATWALLA[6]: It appears to me that the acid radical should be considered a factor. We are comparing a sulfate solution with a chloride solution and a nitrate solution and are totally disregarding the acid radical phase. Prof. Watts, how pure were the metals you used? Some of these metals are obtainable commercially in a much purer condition than others, and very small amounts of impurities have a decided effect on the results.

O. P. WATTS: In regard to the question of chromium, it was the Goldschmidt (Al reduced oxide) variety. We bought it in Germany before the war. The tungsten was a bar of General Electric Co's pressed tungsten. The molybdenum was the Goldschmidt brand. The silicon was the Carborundum Company's "commercially pure silicon," probably containing around 97 per cent silicon.

COLIN G. FINK[7]: In other words, in all of your metals there is at least a half per cent of impurity.

O. P. WATTS: Yes, in the case of silicon, of course, much more than that. The effect of the acid radical is brought out in the case of duriron, which will resist sulfuric acid satisfactorily, but is attacked by hydrochloric acid; in applying these tests the acid radical has to be taken into consideration.

A. L. FERGUSON[8]: The title of the paper refers to corrosion-resisting alloys, and, as I understand from the discussion, pure metals were used in the tests, I do not see the connection between the tests applied to pure metals and their application in the case of alloys.

O. P. WATTS: The tests were carried out on this list of about 40 alloys, which Kurtz and Zaumeyer found to be resistant in the

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[8] Asst. Prof. of Physical Chemistry, Univ. of Michigan, Ann Arbor, Mich.

copper sulfate test. In the main they were alloys of iron with 8 per cent or more of chromium, and also in many cases molybdenum, nickel, copper and other non-ferrous alloys were included in the lists, besides those that Kurtz and Zaumeyer had already tested. Then these few elements specifically mentioned were tried in addition to this list of alloys, so that the test of the elements is merely a little supplementary matter.

R. J. McKay[9]: I would like to corroborate the statements on the effect of different acid radicals. Our experience in corrosion testing has shown that results with nickel alloys using sulfuric acid cannot possibly be applied to hydrochloric acid, even though concentration, temperature and other conditions are identical. The difference in corrosion loss is much greater between these two mineral acids than that between two such acids as acetic and oxalic.

[9] Supt. of Technical Service, International Nickel Co., New York.

A paper presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 2, 1924, Dr. Saklatwalla in the Chair.

INSOLUBLE ANODES FOR ELECTROLYSIS OF BRINE. THE LEAD-SILVER SERIES.[1]

Preliminary Note.

By Colin G. Fink[2] and Li Chi Pan.[3]

Abstract.

Anodic corrosion tests are presented for the alloys of the system silver-lead, and it is shown that the corrosion loss in brine drops very abruptly upon the addition of small percentages of silver to lead, or *vice versa*. The voltage curve is similar to the corrosion loss curve.

Although the lead-silver series has been carefully investigated in the past as to crystallographic structure and fusion point,[4] no systematic studies of the corrosion resistance of this series of alloys has, to date, been recorded.

Lead has a very strong affinity for silver, and alloys with it in all proportions. However, certain precautions must be observed during casting, in order to get uniform composition. Levol[5] refers briefly to the corrodibility of a few of the silver-lead alloys. The alloy corresponding approximately to the formula Ag_4Pb, he finds is readily corroded by moist air. Similarly, the alloy corresponding to the formula $Ag_{12}Pb$. The work of Bauer,[6] and others, would likewise lead one to believe that alloys of the system Ag-Pb are very unstable. In spite of these discouraging reports, we

[1] Manuscript received May 30, 1924.

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[3] Graduate Student, Chem. Engineering, Columbia Univ.

[4] Heycock and Neville (1897), Philosoph. Transact., **198**, A, 137 (1897); Friedrich, Metallurgie, **3**, 396 (1906); G. J. Petrenko, Z. anorg. Chem., **53**, 200 (1907).

[5] Ann. chim. phys. (3) **39**, 163 (1853).

[6] Berichte, **4**, 453 (1871).

undertook the study of the system, employing the forced corrosion test described by Fink and Eldridge.[7]

In the selection of an anode that will satisfy all the requirements for the electrolysis of brine, and also show improvements over the anode now being used in the industry—

1. The anode material must resist oxidation or attack by such substances as sodium chloride, hydrochloric acid, hypochlorous acid, chlorine gas and other oxidizing agents.

2. The anode material must have mechanical strength.

3. The anode material must have a low electrode potential or a low chlorine overvoltage.

4. The anode material, if it should go into solution or corrode, must not contaminate nor affect the product or products.

5. The anode material must be a good electrical conductor.

Since there is no single metal, or non-metal, that will satisfy all of the above requirements, attention has been directed to alloys, particularly to the alloys made of common metals which are least soluble under the conditions prevailing. Lead, silver, and mercurous mercury, form insoluble chlorides. After some preliminary experiments with lead-silver anodes, it was observed that a coat consisting largely of oxides, instead of chlorides, was formed over the anodes. The preliminary experiment with lead-mercury anodes was unsuccessful, but, by accident, an alloy of lead with an extremely low content of mercury was obtained and tested. The result indicated possibilities in the lead-mercury brinary system and in the lead-silver-mercury ternary alloys.

With these ideas in mind, the following schedule of experimental work was adopted. In each case the electrolytic corrosion loss of the anodes in a 5 per cent brine was to be determined. With the exception of I, diaphragms were to be used.

I. Lead-silver series, without diaphragm, at 22° C.
II. Lead-silver series, with diaphragm, at 22° C.
III. Lead-silver series, at 80° C.
IV. Lead-silver-manganese series, at 80° C.
V. Lead-mercury series, at 80° C.
VI. Lead-silver-mercury series, at 80° C.

[7] Trans. Am. Electrochem. Soc., 40, 51 (1921).

VII. Lead peroxide series, at 80° C.

(a) Pure lead peroxide.
(b) With silver.
(c) With manganese dioxide.
(d) With silver and manganese dioxide.

Preparation of Anodes. The anodes of the present report were made of pure lead and pure silver, melted in a small electric furnace and cast into a graphite mold to a uniform size of 0.6 x 1 x 9 cm. The surface exposed to the electrolyte was approximately 25 sq. cm.

The apparatus used is similar to that used by Fink and Eldridge,[8] except that the cells were arranged in cascade, and for the 80° C. tests an electrical heating system was added. Porous clay cups were used as diaphragms, and anolyte and catholyte separately circulated. The cathodes were made of sheet iron, 8.9 x 14.6 cm. Circulation of electrolyte was provided through the cells in series, the direction of circulation being reversible. Copper coulometers were used.

Test Proper. The electrolyte was prepared from pure sodium chloride, 5 per cent by weight. About 150 liters of it were kept in a glass reservoir, from which it was made to circulate through the cells, and back to the reservoir by an air-lift, at a rate of 3 liters per hour; direction reversed twice daily. The current density was kept at 15 amp. per sq. ft. (1.6 amp./sq. dm.). All the cells were in series. The test was run for three weeks, after which the anodes were cleaned, dried and weighed and corrosion losses determined. The results are plotted in Fig. 1 and 2 and are based on readings of about 100 anodes. A typical experiment is recorded in Table I.

Tests are still in progress, and this report is to be understood merely as a preliminary announcement.

Referring to the curves of Fig. 1 and Fig. 2, it is striking how sharply the corrodibility of silver or of lead drops upon the addition of small percentages of the second metal. In this respect the curves are similar to those for lead-thallium in sulfate electrolytes.[9] It is also apparent that with rise in temperature or

[8] *Loc. cit.*
[9] Fink and Eldridge, *loc. cit.*

rise in current density the anodic solubility of the lead-rich alloys increases at a decidedly faster rate than that of the silver-rich alloys.

An interesting point in the low temperature-low current density corrosion and voltage curves is the kink at about 2 per cent silver. This kink corresponds closely to the eutectic point in the melting point curve. A similar observation has been made in the study of a number of other alloys.[9]

TABLE I.

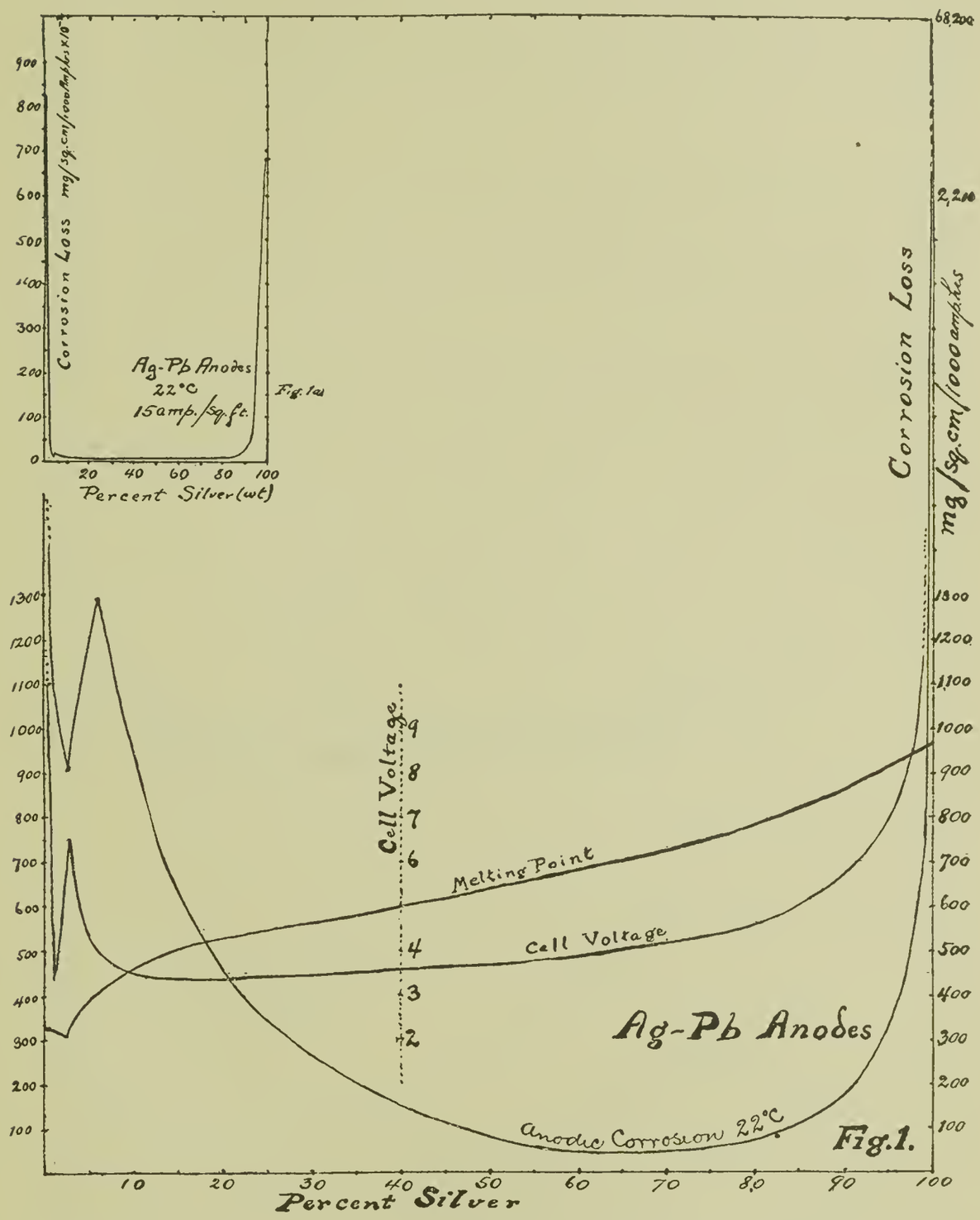
Lead-Silver Alloys.

Duration of test, 510 hours. Current density, 15 amp. per sq. ft. (1.6 amp./sq. dm.). Cathodes, iron. Electrolyte, 5 per cent NaCl. Temperature, 22° C. Clay diaphragm.

Anode Per cent Ag	Anode Loss Mg/sq. cm./1,000 amp. hr.	Average Cell Voltage
0.0	82,400.0	Over 16.0
1.0	1,100.0	3.4
2.25	914.0	6.5
5.47	1,290.0	3.65
11.40	457.0	3.4
18.24	476.0	3.5
25.78	311.0	3.5
34.20	188.0	3.5
43.83	156.0	3.67
54.90	46.8	3.4
67.60	521.6	4.42
82.40	98.0	4.52
100.0	68,200.0	Over 16.0

It is a well-known fact that the solubility of a number of metals in acids decreases as the purity of the metal increases. Thus, for example, zinc 99.99 per cent pure is very insoluble in acids as compared with zinc of 99 per cent and 98 per cent grade. It would have been expected, therefore, that the purer the silver, that is, the lower the lead content, the more insoluble the metal. But submitting silver and the silver-lead alloys to anodic corrosion in brine, we find the exact opposite. That is, a small proportion of lead added to the silver, or a small proportion of silver added to the lead, reduces the solubility to less than 1 per cent of the solubility of the pure metal.

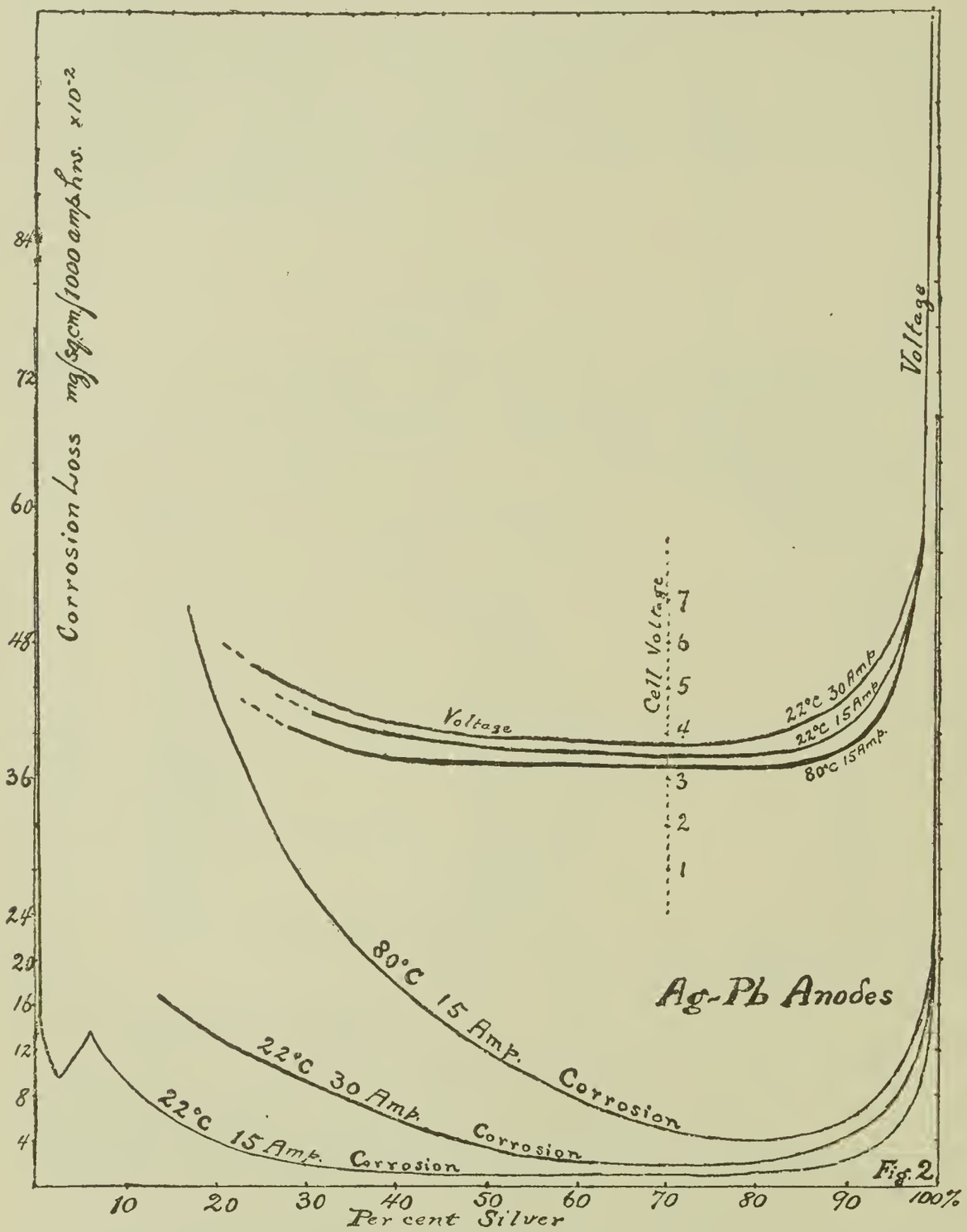
This apparent discrepancy between ordinary chemical corrosion in acids (where pure metals are more resistant) and anodic



Anodic Corrosion and Cell Voltage at 22° C. of Silver-Lead Alloys in 5 Per Cent NaCl Solution.

corrosion (where alloys are more resistant) may be due to the relative velocities of the reactions taking place on the surface of the metal or alloy. The film or scale on the silver-lead anodes

consists largely of peroxide of lead (PbO_2), *not* chloride, and chloride of silver (and possibly some oxide of silver). We found



Effect of Increase in Temperature of Electrolyte and Increase in Current Density on Anodic Corrosion Loss of Silver-Lead Alloys.

no appreciable quantities of chloride of lead present. This film apparently catalyzes the formation of molecular chlorine in preference to the formation of metal chlorides. This case is similar to

that of the copper silicide anode,[10] where the surface film catalyzes the formation of gaseous oxygen in preference to the formation of metal sulfates.

INTERPRETATION OF RESULTS AND CONCLUSIONS.

From the experimental data so far collected, the following conclusions may be drawn:

1. An alloy of lead and silver resists anodic corrosion in brine much better than either of the metals alone.

2. The alloy which gives the best results contains about 60 to 80 per cent silver by weight.[11]

3. A certain relation between the corrosion curve, voltage curve, and the fusion curve of the lead-silver series is apparent.

4. The anodic corrosion of lead-silver alloys gives rise to a film, consisting largely of oxides instead of chlorides, over the anode surface. The extent of corrosion is primarily determined by the physical nature of this film, which appears to catalyze the formation of chlorine gas. The more dense and adherent, the less will be the corrosion. Corrosion losses are much greater in those anodes having a fresh surface and decrease as the film builds up, until corrosion loss is practically constant, when the maximum protection from the film is reached.

5. The anode corrosion of lead-silver alloys at 30 amp. per sq. ft. (3.2 amp./sq. dm.) is more than twice as high as that at 15 amp. per sq. ft. (1.6 amp./sq. dm.).

6. The anode corrosion of lead-silver alloys at 80° C. is greater than that at room temperature.

Columbia University,
New York City,
May 30, 1924.

DISCUSSION.

COLIN G. FINK: I may add that the point that Mr. Pan and I wished to bring out most emphatically is this: If you had relied upon the text book data of the solubility of lead, and of the solu-

[10] Fink, Ind. Eng. Chem., **16**, 566 (1924).
[11] Pats. applied for and assigned to Bario Metals Corp., N. Y. City.

bility of silver in hydrochloric acid, or in sodium chloride solutions, you would not have been tempted to try out an alloy of these two metals as an anode in the brine solution used in the alkali cells. The other point we wish to bring out is that when it comes to forced corrosion tests, such as the electrolytic, we can actually reverse results. That is to say, metals or alloys which stand up well under atmospheric corrosion conditions, will on the other hand go into solution readily by this forced electrolytic test, and conversely there are alloys which will stand up remarkably well under the forced electrolytic test, but go to pieces on the slow atmospheric corrosion test.

Accordingly, here again we have a case where you cannot use the atmospheric corrosion test as a final test. It just emphasizes the point that Prof. Watts brought up: "A forced test may help to eliminate a large number of alloys and concentrate your attention upon a few alloys." Of course, in testing for corrosion resistance as we have in the case of silver-lead alloys we have tried to approach the actual service conditions as closely as possible.

It would have been almost useless to take a lot of silver-lead alloys or other alloys and just immerse them in sodium chloride solution or submit them to the salt spray test. You would find that the very alloy we know shows low anodic losses did not stand up, because no doubt the film is not built up properly or the film is destroyed upon boiling the sodium chloride solution. With applied electromotive force you maintain or continually build up, so to speak, this protective film. When we talk of protective films it is absolutely necessary to know under what conditions those protective films are formed or are to function. The point of erosion enters there too, and often a protective film behaves better, due to its hardness, due to its ability to resist the flow of the solution over the surface, than another film which may be better from a chemical point of view. This is observed frequently in turbine-blade tests.

A. L. Ferguson[12]: May I ask the authors if the potential was increased materially by this film?

Colin G. Fink: It is just the other way round. The potential of the pure metals, if you look at Fig. 1, or better still at Table I,

[12] Asst. Prof. of Physical Chemistry, Univ. of Michigan, Ann Arbor, Mich.

is decidedly higher, it is over 16. The moment you build up this catalytic film, that is, the moment you discharge the chlorine readily, your potential drops. The potential curve and the corrosion curve run parallel. In practically all of our experience so far, you can not have low anodic corrosion losses and high voltages with the same alloy. An insoluble anode made of very soluble metals may have a very low potential. That is fortunate as far as commercial application goes. Various alloys proposed, that show a low solubility under ordinary chemical conditions, for example, a 75 per cent silicon-iron alloy, have a voltage of 5000 or more. The interesting point is that you can build up a catalytic film on a very soluble metal or alloy, and you not only reduce the solubility but you reduce the voltage at the same time.[13]

[13] J. Ind. Eng. Chem., **16**, 566 (1924).

A paper presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 2, 1924, Dr. Saklatwalla in the Chair.

NOTES ON CORROSION TESTING BY DIFFERENT IMMERSION METHODS.[1]

By Henry S. Rawdon[2] and A. I. Krynitsky.[3]

Abstract.

The need for choosing a corrosion test which shall in some measure approximate the service conditions is emphasized and illustrated by reference to an unusual case of corrosion in a submarine cable. The general types of immersion tests, simple or total immersion and two kinds of repeated immersion, continuous and intermittent, are described and illustrated as to the apparatus needed. Test results for a series of chromium steels in immersion tests of the simple and repeated type in distilled water, as well as immersion in dilute hydrochloric acid and citric acid, are given. In general, the chromium steels are more resistant to the intermittent immersion than to simple immersion in distilled water—a phenomenon which appears to be associated with the formation of a protective film over the surface of the specimen.

I. INTRODUCTION.

It is evident that there is no "all-round" corrosion test. The immersion test in some form is, perhaps because of the relative ease with which it can be carried out, the favorite method of corrosion testing. Immersion tests, however, must be carried out with due regard for the particular sample under observation. For example, a sheet of tin, containing a slight amount of aluminum as an impurity, when immersed in water or dilute sodium chloride solution, becomes so brittle by internal corrosion in the

[1] Manuscript received July 16, 1924. Published by permission of the Director of the Bureau of Standards, Washington, D. C.

[2] Physicist, Bureau of Standards.

[3] Associate Physicist, Bureau of Standards.

course of a few days or weeks that it can be crumbled in the fingers. This, of course, has a very different significance from the results obtained when a sheet of "tin plate" is tested in a similar way.

Although the immersion test is often of great value in demonstrating changes due to corrosion when conditions are such as will permit electrolytic action to occur, as in coated metals, soldered joints and the like, it is the more strictly "chemical" aspect of corrosion that the authors have in mind in this paper. The results given here are not in the nature of a completed investigation, and are presented as much for the discussion which may be stimulated as for their own possible value.

II. GENERAL PRINCIPLE GOVERNING THE CHOICE OF TEST.

In general, the practical user is interested not so much in the "why" of the corrosive conditions which confront him, as in their control or, perhaps more strictly speaking, in the choice of suitable materials to withstand the conditions which must be met. First of all then, any test must be related to the service conditions. In fact, a full-scale service test, such as is now under way at the Bureau of Standards in the soil corrosion investigation, appears to be the only answer at times.

A case of failure in service recently brought to the Bureau's attention illustrates admirably this point of the choice of the proper preliminary test.[4] Submarine telegraphic cables, as a rule, do not cause much concern from corrosion troubles. Although a "protective" layer usually covers the galvanized low-carbon steel wires, which are closely wound spirally around the cable for strengthening it, complete protection from contact with the sea water is not afforded. In the deep sea water, where the oxygen content is low and temperature and other changes are slight, corrosion of the steel takes place very slowly, and usually very uniformly over the exposed surface. Fig. 1 shows, however, the broken end of a cable, and illustrates marked localized corrosion, although it should be stated that 15 years elapsed before service was interrupted from this cause. The probable cause of the failure of the cable is not the point to be emphasized here, but rather the

[4] The authors are indebted to Dr. H. L. Curtis, Bureau of Standards, for the example described here.

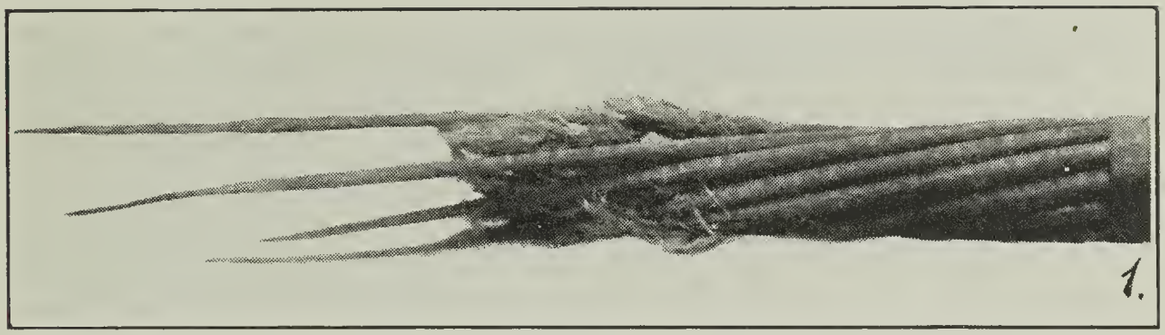


Fig. 1. Corroded End of a Submarine Cable Removed from Service. x ½. Note the decidedly local character of the corrosion of the steel wires. The outer jute covering has been removed.

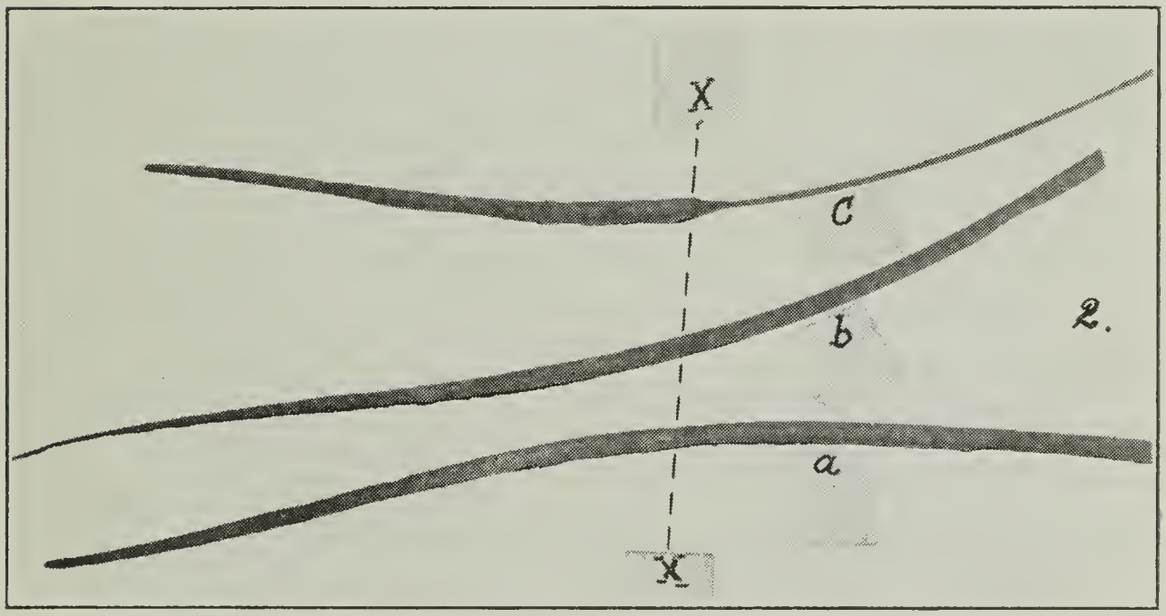


Fig. 2. Appearance of Steel Wires from the Cable of Fig. 1. After Immersion in Hydrochloric Acid. x 1. Three wires were removed from the corroded cable end and the sound ends immersed in 10 per cent acid solution up to the point shown by line X-X. The portion of the wires to the left of this line were corroded in service, to the right of the line in the acid solution.

Fig. 5. Apparatus for the Repeated Immersion Test.

pronounced difference in the properties of some of the steel strengthening wires used in this cable, all of which, however, behaved essentially the same under the conditions encountered in service.

Fig. 2 shows the results obtained when three of the corroded steel stay wires, chosen at random, were removed from the cable end and were freely suspended in dilute hydrochloric acid (1 vol. conc. HCl, 9 vol. H_2O). The end of the wire immersed in the acid was that opposite the one which failed in service, and in each case as unwrapped from the cable showed only relatively slight corrosive attack on the part subsequently immersed in the acid solution. The marked difference in the resistance of the three wires to the acid was striking. Had this or a similar test for determining the relative solubility been carried out on these wires at the time of the manufacture of the cable, there is no doubt whatever that wire 'C' (Fig. 2) would have, *a priori,* been classed as inferior, and as unsuitable material for the purpose; whereas, the inspection of the cable made after 15 years of service did not indicate that this wire was any more unsuitable for this service than either of the other two examined.

III. IMMERSION TESTS.

For certain types of service, immersion tests will often give the information required to guide one in the choice of the proper material for withstanding the corrosive conditions involved. This applies particularly to some of the chemical industries. Such tests may be, (1) of the simple total immersion type, in either aerated or unaerated solutions, (2) accelerated solution tests by electrolytic means, or (3) immersion tests of the intermittent type.

Simple Immersion.

There is shown in Fig. 3 a convenient arrangement for carrying out tests of this character. Although, "on paper," the test consists merely in noting the change in appearance and weight after immersion for a stated length of time within any corrosive liquid decided upon, the actual technique of the test is not nearly so simple as this would imply. In the apparatus shown in Fig. 3 the bottles containing the corrosive solution with a test specimen freely suspended in each are partially immersed in the water in

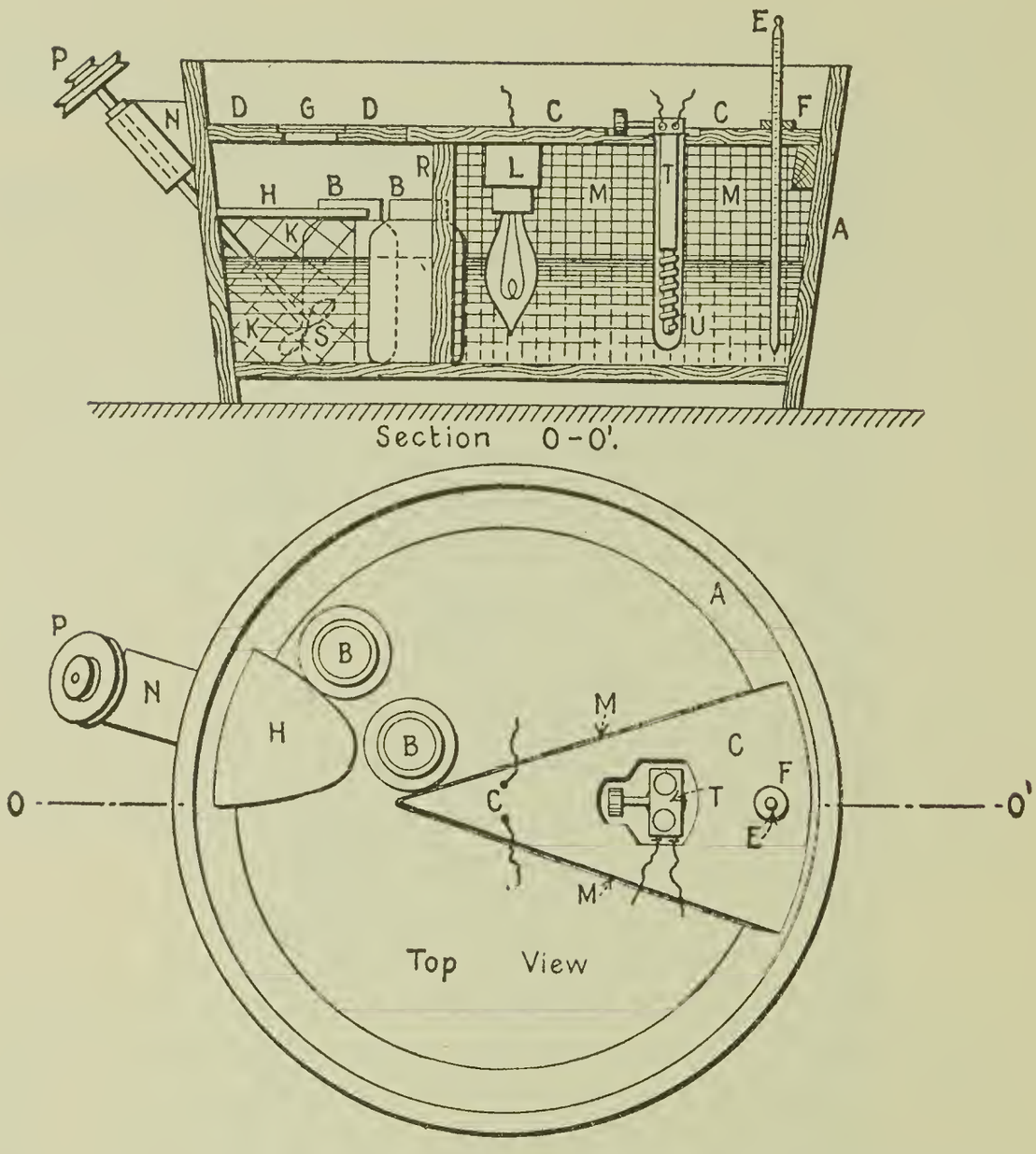


FIG. 3. Diagram of Apparatus for Conducting Corrosion Tests for Simple Immersion at Constant Temperature.

A—Wash tub.
B—Bottles containing corrosive medium.
C—Stationary section of wooden cover.
D—Removable portion of this cover. It is not shown in the top view.
E—Thermometer.
F—Cork supporting thermometer.
G—One of two glass windows of the removable part D.
H—Wooden board to protect bottles from splashing water caused by stirrer.
K—One-inch wire screen attached to the edges of board H and surrounding stirrer S.
L—Electric lamp used here as heater.
M—Wire screen attached to edges of stationary section C and protecting lamp, thermostat and thermometer.
N—Support for axle of stirrer.
P—Pulley attached to axle of stirrer.
R—Wooden support on which the front part of C is at rest.
S—Stirrer.
T—Thermostat.
U—Glass housing for thermostat. It should contain glycerine for conducting heat.

the bath, the temperature of which is maintained by the lamp and controlled by the thermostat, as shown.

Although statements have been published[5] to the effect that aeration of the corroding solution produced no accelerating effect, at least in the particular cases discussed, it is usually considered desirable to control this variable, either by saturating the solu-

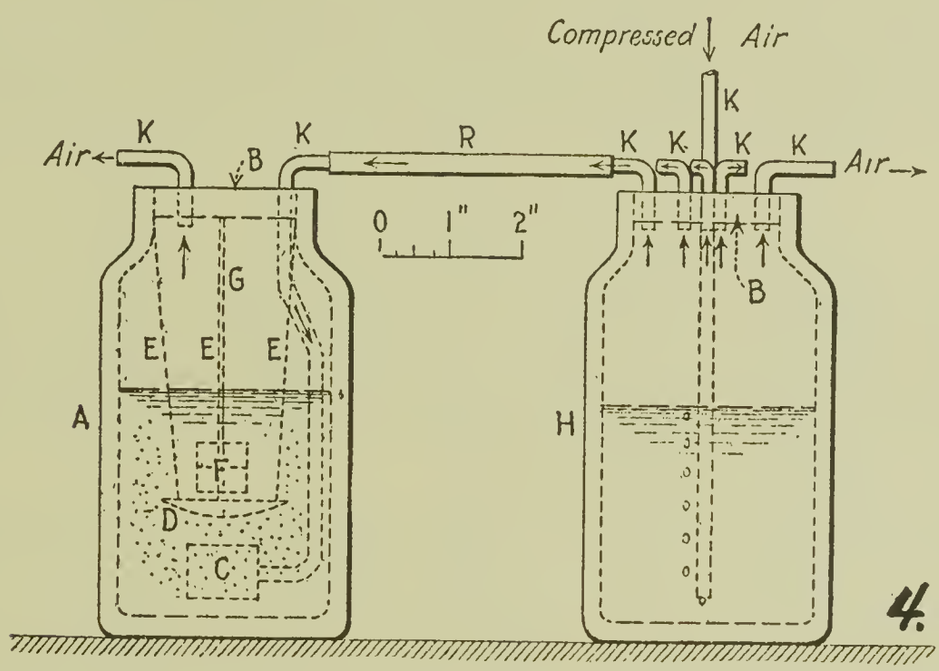


FIG 4. Method of Aeration Used in Simple Immersion Corrosion Tests.

A—One of five bottles forming a unit.
B—Cork.
C—Porous alundum cylinder hermetically sealed at both ends in such a manner as to permit access to compressed air only.
D—Watch glass used here as baffle plate.
E—Threads by which D is suspended. They are attached to D by means of Khotinsky cement.
F—Specimen.
G—Thread to suspend specimen.
H—Bottle distributing compressed air to five bottles of the unit. It should contain water or corrosive solution.
K—Glass leads.
R—Rubber connections.

tions with air or by excluding the air as much as possible. In case aeration of the solutions is desired the arrangement shown in Fig. 4 for supplying air to the different bottles, is placed within the constant temperature bath, and precautions should be taken as shown in the illustration, for breaking up the air bubbles into a host of tiny ones as they pass through the solution, and also for preventing direct contact between the specimens under

[5] Anderson, R. J., and Enos, G. M., An Accelerated Electrolytic Corrosion Test, preprint Am. Society Testing Materials, 1924.

test and the air bubbles used for saturating and agitating the solutions.

Sometimes it is desirable to accelerate simple immersion tests. For most metals this can be done by application of a small external e. m. f. to a cell, in which the specimen is made the anode, a resistant metal such as platinum, the cathode, and the solution under test the electrolyte. Anderson[6] has obtained results which show that, in the majority of cases tried, there was a close parallelism between results obtained in this way and in those from simple immersion of the same specimens in similar solutions.

Intermittent Immersion.

Some materials in service are exposed to the attack of a corrosive medium intermittently; instances of this type of service are illustrated along any wharf at the seashore where total immersion occurs twice a day during high tide, alternating with atmospheric exposure during low tide.

Intermittent immersion tests, as carried out in the laboratory, may be of two kinds: (1) a simple repeated immersion in which the specimens are dipped momentarily into the solution and then withdrawn into the air so as to allow them to drain off, the cycle being repeated indefinitely; (2) an interrupted repeated immersion, in which the driving mechanism is automatically stopped after the specimens are withdrawn from the solution, and they are held in the air long enough to permit them to dry. Fig. 5 shows a form of apparatus developed at the Bureau of Standards for the simple repeated immersion test. It consists essentially of 1/20 h. p. electric motor, which by means of a worm and reducing gears drives a series of crank arms at a slow speed. One-third r. p. m. has been found satisfactory in conducting this test. The specimens, attached to a horizontal rod, fastened to the end of the vertical crank arms, are actuated by the crank so as to be alternately lowered into the solution and then immediately raised into the air.

The degree of aeration in this type of test is as complete as it can be made, and no attempt is made to vary or change it. A suitable and convenient device for interrupting the working of

[6] Anderson, R. J., and Enos, G. M., An Accelerated Electrolytic Corrosion Test, preprint Am. Society Testing Materials, 1924.

the driving mechanism to permit the holding of the specimen, after immersion in the liquid, in the air for any period desired up to approximately 1 hour has been described elsewhere by the authors.[7]

TABLE I.

*Composition of Chromium Steels Used.**

Series No.	C Per cent	Mn Per cent	P† Per cent	S† gravim. Per cent	Si Per cent	Cr Per cent
25	0.16	0.02	0.007	0.036	0.10	5.82
26	0.16	0.02	....	....	0.48	11.37
27	0.23	0.02	....	....	0.50	15.78
28	0.28	0.02	0.007	0.055	0.22	7.10
29	0.32	0.02	....	....	0.20	9.32
30	0.39	0.02	....	....	0.28	13.91
31	0.23	0.01	....	....	0.15	3.63
32	0.52	0.02	....	....	0.43	7.68
33	0.26	0.01	....	....	0.25	10.51
34	0.69	0.02	....	0.030	0.46	2.66
35	0.84	0.01	0.013	0.038	0.39	4.31
36	0.74	0.02	....	....	0.31	6.03
37	0.12	0.02	0.004	0.073	0.22	9.81
38	0.06	0.02	....	....	0.30	19.66
39	1.44	0.01	....	0.041	0.47	10.60
40	0.98	0.02	0.005	....	0.43	15.91

* Analysis by H. A. Bright, associate chemist.

† Sulfur and phosphorus determinations were made on only a limited number, as the work of preparing the steels progressed, as a check on the purity of the raw materials.

IV. COMPARATIVE RESULTS OF IMMERSION TESTS ON CHROMIUM STEELS.

The difference in the results obtained with similar specimens in simple immersion, as compared with repeated immersion, is sometimes striking, even for such resistant materials as high chromium steels. No results are available with the intermittent repeated immersion tests as the tests on these materials were started before this particular type of apparatus was available, so that the comparison here will be made only with the simple immersion and the continuous repeated immersion. The specimens used were a series of special steels prepared at the Bureau of Standards,[8] the compositions of which are given in Table I.

[7] Rawdon, Krynitsky and Finkelday, Types of Apparatus Used in Testing the Corrodibility of Metals, preprint Am Society Testing Materials, June, 1924.

[8] These were made by means of the high-frequency induction furnace by R. P. Neville, associate chemist (deceased) and Louis Jordan, chemist.

Immersion Tests in Distilled Water.

The immersion tests of the simple and repeated type were carried out at room temperature (10° to 15° C. approx.) in distilled water, with polished rectangular prismatic specimens, the surface area of which varied from 6 to 13 sq. cm. The simple immersion test was run without aeration, although the water was

TABLE II.

Method Used for Grading the Chromium Steels after Corrosion.

Grade	Approximate time before rust appeared		Approximate area corroded after 30 days Per cent
	Days	Hr.	
1	....	1-1.5	50
2	....	2.5-5	50
4	....	17-24	50
6	....	1-1.5	33
8	2-3	.....	50
10	4-7	.....	50
12	13	.....	50
14	....	1-1.5	5
16	....	2.5-5	5
18	....	17-24	5
20	2-3	.....	5
25	4-7	.....	5
30	13	.....	5
32	....	1-1.5	Trace
34	....	2.5-5	Trace
36	....	17-24	Trace
38	2-3	.....	Trace
45	47	.....	Trace
50	13	.....	Trace
60	150	.....	Trace
70	265	.....	..
75	280	.....	..
80	340	.....	..
85	400	.....	..
90	466	.....	..
100	512	.....	..

renewed frequently in order to keep the volume up to 300 cu. cm. This same volume was used in all the other types of test also. Both annealed and heat-treated specimens were used. The annealing was carried out at 750° C.; the heat treatment consisting in quenching from 1,015° C. in cold water, with a subsequent tempering at 180° C. The necessary identification marks were put on tags attached to the silk-thread suspensions, rather than

on the steel specimen. At the completion of the test specimens were graded arbitrarily with respect to their resistance to corrosion. A grade of 100 was used for those specimens which remained unattacked at the close of the test. The time required for the appearance of the first rust spots, and the relative extent of the rusted areas after 30 days' test, were used as the criteria for judging the specimens which were of relatively low resistance. Those which proved much more resistant were classed simply according to the time required for the first rust to appear, although the appearance of the specimen after this time was also noted and recorded. In Table II is given the method of grading used. It will be noted that below grade 50 the specimens were graded rather closely. The relative order of arrangement of the corroded specimens, according to this method of grading, is given in Table III.

The conclusions drawn from these tests concerning the relative value of different compositions serve mainly to confirm those of other investigators; that is, hardening by heat treatment is generally accompanied by superior corrosion resistance; a chromium content of 11 per cent or more and approximately 0.35 per cent carbon appears to be necessary for high corrosion resistance. An increase in the carbon content is associated with reduced resistance to corrosion. The difference in the results obtained with the two types of immersion tests are believed to be of value, and to be of real significance as to the difference in the behavior of these steels, which may be expected in different kinds of service which approximate total or intermittent immersion in water.

Surface Films.

Some observations made in the course of the tests are of interest, and possibly of significance, in accounting for the relatively higher "life," as a whole, obtained in the repeated immersion tests. A grayish-white flocculent substance was noted in the distilled water in a number of cases, after the test had progressed 15 to 25 days. In some cases, this had a thin flaky form, and can hardly be attributed to a film separating from the surface of the glass bottle, as it was observed in numerous cases that such a film was present on the surface of the metal specimens themselves, and these were freely suspended and had no contact with

TABLE III. *Chromium Steels Arbitrarily Graded on Scale of Table II after Immersion in Distilled Water.*

Series No.	Cr Per cent	C Per cent	Annealed. Physical state before test	Grading	Quenched. Physical state before test	Grading
			Simple immersion test			
34	2.66	0.69	Sound	1	Cracks	1
31	3.63	0.23	Surface crack	1	Cracks	1
35	4.31	0.84	Sound	1	Cracks	6
25	5.82	0.16	Surface cracks	1	Cracks	14
36	6.03	0.74	Sound	1	Cracks	18
28	7.10	0.28	Sound	6	Cracks	32
32	7.68	0.52	Cracks	1	Cracks	32
29	9.32	0.32	Sound Cracked	75 6	Cracks	38
37	9.81	0.12	Sound	25	Sound	80
33	10.51	0.26	Sound	90	Deep cracks	18
39	10.60	1.44	Sound	1	Deep cracks	25
26	11.37	0.16	Sound	70	Cracks	38
30	13.91	0.39	Sound	100	Deep cracks	100
27	15.78	0.23	Sound	100	Crack	100
20	15.91	0.98	Surface crack	60	Deep cracks	60
38	19.66	0.06	No cracks. Dark streak of inclusion	45	Sound	100*
			Repeated immersion test			
34	2.66	0.69	Sound	4	Deep crack	36
31	3.63	0.23	Surface crack	14	Surface crack	36
35	4.31	0.84	Sound	2	Deep crack	38
25	5.82	0.16	Surface crack	18	Deep crack	38
36	6.03	0.74	Sound	2	Deep crack	85
28	7.10	0.28	Crack	18	Deep cracks	100
32	7.68	0.52	Very deep cracks	14	Deep crack	50
29	9.32	0.32	Sound	36	Deep crack	100
37	9.81	0.12	Sound	100*	Sound	100*
33	10.51	0.26	Sound	100	Deep cracks	100
39	10.60	1.44	Sound	16	Sound	80
26	11.37	0.16	Sound	100	Deep crack	100
30	13.91	0.39	Deep crack	100	Deep crack	100
27	15.78	0.23	Sound	100	Sound	100
20	15.91	0.98	Sound	80	Deep crack	100*
38	19.66	0.06	Sound	80	Sound	100*

* These series were graded 100 conditionally, since they had been tested for only 400 days when the last observations were made.

the glass. The most significant feature concerning the film, however, was its more frequent occurrence on the specimens used in the intermittent immersion test. The number of cases in which it was observed to any appreciable extent in the simple immersion series was considerably less than for the other series. Suffi-

cient samples of the material (0.002 to 0.003 mg. after drying) were obtained after the test had progressed for 140 to 160 days for several of the annealed specimens for a qualitative chemical analysis[9] to be made. The specimens themselves showed no evidence of rust at the time. Silicon and iron were both reported as present in the film substance, but chromium was not detected in any case. This was true for the samples taken from both types of immersion tests.

Whether the formation of a film of this kind over the surface of the specimens is of significance, and will account for the superior resistance of the specimens to the repeated immersion as compared with simple immersion, is somewhat problematic. That there is a difference, which is sometimes pronounced with certain specimens, was readily demonstrated by subjecting the same specimen to the two tests in succession. The results obtained confirmed the conclusion that, for the conditions used, the simple immersion test was decidedly the more severe of the two.

Acid Immersion Tests.

In spite of much which has been said to the contrary, the idea persists with many that high chromium or "stainless" steels are likewise of necessity acid resisting in their properties. A series of simple immersion tests in $N/2$ hydrochloric acid solution, and in 10 per cent citric acid, were carried out, the latter being used as representative of the "strongest" fruit acid which such steels would probably have to withstand. Lemon juice, according to Thorp,[10] has a citric acid content of approximately 6.8 per cent. The tests were carried out at room temperature (approx. 20° C.) for the hydrochloric acid series and at 27° $\pm$ 0.5° C. for the citric acid, the apparatus shown in Fig. 3 being used for the latter. Annealed specimens only were used, as in quenching the high chromium steels cracks often form, and thus "loss-of-weight" determinations on such specimens after corrosion may be misleading, since it is impossible to measure or even estimate the area corroded.

A sufficient number of specimens, usually 6, were immersed initially at the same time, so as to permit one to be removed for

[9] This was made by J. A. Scherrer, associate chemist.
[10] Thorpe, Dictionary of Applied Chemistry, Vol. III, p. 311.

weighing at the end of each observation period (either 24 or 48 hours). A volume 300 cu. cm. of the solution was used for each specimen. The loss of weight per unit area per unit time was then determined.

In Table IV are summarized the results obtained in the immersion tests in $N/2$ hydrochloric acid. The results obtained for similar specimens immersed in citric acid are summarized in Table V.

TABLE IV.

Relative Order of Resistance of Annealed Chromium Steels.

Immersed in $N/2$ HCl solution, 168 hr., room temperature, approx. 20° C.

Series Number	Cr Per cent	C Per cent	Average loss in weight mg. per sq. cm. per hr.
31	3.63	0.23	0.07
34	2.66	0.69	0.08
28	7.10	0.28	0.09
29	9.32	0.32	0.11
25	5.82	0.16	0.14
37	9.81	0.12	0.21
38	19.66	0.06	0.37
35	4.31	0.84	0.54
36	6.03	0.74	0.54
26	11.37	0.16	0.55
32	7.68	0.52	0.57
33	10.51	0.26	0.63
40	15.91	0.98	0.63
39	10.60	1.44	0.69
27	15.78	0.23	0.74
30	13.91	0.39	0.87

The results obtained by immersion in hydrochloric acid indicate that the resistance to acid attack is dependent upon the chromium and the carbon contents. An increase in either tends to lower the resistance of the alloy.

The influence of composition upon the resistance to citric acid attack is not so evident. However, many of the apparent exceptions are to be attributed in all probability to the physical condition of the specimens. If a conclusion is based upon the "sound" specimens in Table V, it appears that the order of resistance is, in general, different from that in Table IV. Alloys high in chromium resist the attack of the acid better than those lower

in this element, although carbon also plays a part, apparently by lowering the resistance, as it is increased in amount.

So far as the present article is concerned the principal conclusion to be drawn from these tests is that the steels differ in their relative resistance to the two acids. The results of one test

TABLE V.

Results of Simple Immersion Test of Chromium Steels.

In 10 per cent citric acid solution for 264 hr. (11 days), 27° ± 0.5° C.

Series Number	Cr Per cent	C Per cent	Average loss in weight per sq. cm. per hr. mg.	Physical state of the surface of specimen before the test
27	15.78	0.23	*	Sound
38	19.66	0.06	0.00	Sound
30	13.91	0.39	0.01	Sound
37	9.81	0.12	0.04	Sound
25	5.82	0.16	0.05	Surface cracks
26	11.37	0.16	0.05	Deep cracks
40	15.91	0.98	0.07	Sound
33	10.51	0.26	0.09	Cracks about 0.8 mm. deep
32	7.68	0.52	0.09	Cracks about 0.8 mm. deep
29	9.32	0.32	0.11	Short crack about 1.6 mm. deep
28	7.10	0.28	0.14	Crack about 3.2 mm. deep
39	10.60	1.44	0.31	Sound
31	3.63	0.23	0.34	Short cracks about 1.6 mm. deep
36	6.03	0.74	0.91	Sound
34	2.66	0.69	1.21	Small cracks
35	4.31	0.84	1.76	Sound

* All specimens of this series show a gain in weight 0.001 g. for whole period of tests, for whole area.

cannot be used as a basis for predicting the probable behavior of the same steels immersed in the other, and furthermore neither one can be used as a reliable basis for predicting the behavior when immersed in distilled water, although some parallelism between the results of the critic acid tests and that in distilled water exists.

SUMMARY.

1. The necessity for suiting a corrosion test to the service conditions is illustrated by tests made upon steel wires, taken

from a submarine cable removed after 15 years' service. Although acid immersion tests showed marked differences in the characteristics of the wires, such as might ordinarily lead one to condemn, as entirely unfit for the service planned, one of the three wires tested, nothing was observed in the cable itself to show that such wires were any more unsuitable in service than those which showed up well in the acid test.

2. Two forms of immersion tests, the simple or total immersion, and the repeated immersion in which the specimen is withdrawn into the air after being dipped into the solution, are discussed and a description of the apparatus for carrying out such tests given. Two forms of repeated immersion and the intermittent type are referred to.

3. The results obtained for a series of chromium steels, varying in chromium content from 2.7 to 19.7 per cent, and with carbon content varying from 0.06 to 1.44 per cent, are summarized to show the differences which occur in the two types of immersion tests in distilled water.

4. The greater resistance observed for the steels tested by intermittent immersion in distilled water, as compared with simple or stationary immersion in the same medium, appears to be associated with the presence of a surface film, which forms more readily under the conditions of the former test than under those of the latter.

5. The results obtained in a series of simple immersion tests of the same chromium steels, in dilute hydrochloric acid and in citric acid, have also been included. These indicate that for the test conditions used, the result of the immersion tests in one acid is not an index of what may be expected in the other, nor of what was found for the same steels in the distilled water test.

DISCUSSION.

R. J. McKay[11]: Dr. Rawdon, on page 364, refers to the acceleration of simple immersion tests. He has shown distinct differences in the results of tests, which are not in themselves very

[11] Supt. of Technical Service, International Nickel Co., New York City.

different; certainly not as different from each other as the applying of an outside e. m. f. from a simple immersion test. Messrs. Fink and Pan pointed out that the application of high e. m. f.'s may change the corrosion of the anode completely. Therefore, I would like to submit my opinion that the application of e. m. f. always causes error. The higher the e. m. f., the greater the error.

COLIN G. FINK[12]: That is not so.

R. J. MCKAY: I believe that any applied e. m. f. would be fatal to drawing true conclusions. Dr. Rawdon quotes the work of Anderson, who obtained results showing a close parallelism between electrolytic acceleration tests and simple immersion tests of the same specimens in similar solutions. Anderson used only one solution, and the results do not necessarily apply to others, but even in this one solution, Anderson's results did not agree very well. They were plotted in curves, which showed a general parallelism between the electrolytic tests and the immersion tests. However, I made a more critical examination of this, as follows:

The simple immersion tests were taken as a criterion, and the percentage errors which would be obtained by the accelerated test were calculated. For instance, if a certain alloy, B, had a rate of 10 in the immersion test and of 14 in the electrolytic test, the error was 40 per cent. These percentage errors were averaged and found to be in the neighborhood of 30 per cent. Thus there was a certain parallelism, but the value for practical engineering conclusions was nil. I also compared monel metal with the other alloys by each test and found that if the question were asked, "Is monel metal better or worse than a certain alloy?" the answer was often in error. Thus a careful analysis of Anderson's results shows them to be an argument against electrolytic acceleration tests rather than for it.

Dr. Rawdon's data are further evidence of the usual erroneous results from accelerated tests. On page 360, Dr. Rawdon says, "When conditions are such as will permit electrolytic action to occur, as in coated metals, soldered joints and the like, it is the more strictly 'chemical' aspect of corrosion that the authors have in mind in this paper." In other words, he draws the distinction

[12] Head, Division of Electrochemistry, Columbia Univ., New York City.

between electrolytic action and chemical action. I would like to concur in that distinction. It is a useful one.

COLIN G. FINK: The Bureau of Standards has for many years strongly recommended the salt spray test, and to me it is a very interesting thing, indeed, to have the Bureau come out and suggest a big improvement over the salt spray test. I wonder what the stainless steel industry would be today if it had depended on the results of the salt spray test. It is true if you work within certain small limits of applied electromotive force, that the tests obtained with the applied electromotive forces are only in a degree different from those without the applied electromotive force, but if you go beyond a certain potential, you will find that you may reverse the results.

Let me illustrate from actual service conditions, where our samples weigh 100 lb. (45.4 kg.) apiece, and where we have tested tons of the alloy. I am referring particularly to the copper silicide alloy we are using as anode at Chuquicamata, in copper sulfate solutions containing sulfuric acid and also a little nitric acid and hydrochloric acid to make it real interesting. At the anode you have two reactions taking place. One reaction is the sulfate ion reacting with water to form oxygen plus sulfuric acid, and the other reaction, the objectionable one, is $SO_4'' +$ metal $=$ metal sulfate. In our case it happens to be $SO_4'' + Cu = CuSO_4$.

Now, without applying any electromotive force, without any applied potential, this latter reaction predominates. However, as you apply an e. m. f. and gradually increase your potential, and as you develop a film on the surface of the anode, which will catalyze the reaction, $SO_4'' + H_2O = H_2SO_4 + O$, then the metal sulfate formation recedes. In practice, as a preliminary step, we hang up the copper silicide anodes in special tanks, to build up the film which will catalyze the oxygen formation in preference to the formation of metal sulfate. If we had depended upon simple acid tests or spray tests for the selection of our anode material, we would be still searching. We must confine our tests to those that approach actual service conditions.

F. N. SPELLER[13]: May I ask Dr. Rawdon if he has any quantitative data on the test shown in Table III.

[13] Metallurgical Engr., National Tube Co., Pittsburgh, Pa.

H. S. RAWDON: All we have is given there in the table, which gives the order of resistance of those steels toward corrosion.

F. N. SPELLER: The specimens were not weighed?

H. S. RAWDON: No, I do not think weight changes would mean anything there.

COLIN G. FINK: As the surfaces were not all the same.

H. S. RAWDON: Some of them were cracked, and you cannot interpret weight changes under such conditions.

F. N. SPELLER: Leave out the cracked ones; most of them are marked sound.

H. S. RAWDON: The increase in weight is very slight, and one couldn't really rely upon it, for drawing definite conclusions—that is for the small specimens which we used. It is the change of surface one is interested in, in stainless steel. We do not care if a stainless steel panel loses, say, a gram a day as long as it stays stainless and bright. Even if it is corroded slightly, as long as it stays bright and stainless I think the user is satisfied.

F. N. SPELLER: This qualitative grading refers only to the appearance?

H. S. RAWDON: Yes.

F. N. SPELLER: There was no perceptible depth of corrosion in the 400 days?

H. S. RAWDON: Suppose we refer to Table III. Take specimen No. 1. "Grade 1" indicates that this specimen showed rust right away, that is, an hour or so after it was put in water, and at the end of 30 days it was half covered with rust.

F. N. SPELLER: At the end of 400 days, what did that look like?

H. S. RAWDON: We did not carry it that far.

F. N. SPELLER: That is where you stopped the tests?

H. S. RAWDON: No, we stopped recording these.

F. N. SPELLER: Are they still under test?

H. S. RAWDON: We have no specimens any longer in solution. We had to tear down the apparatus to move it. The specimens

were allowed to remain in solution in some cases until the solution became muddy from the ferric hydroxide that formed in the solution, and the whole specimen had tufts of rust on it, but we did not make any record of the change of weight.

F. N. SPELLER: Some low chromium steels are highly corrodible; they are not much better than ordinary steel in water, whereas we know the higher chrome steels are very resistant. Now the question is, are you not favoring the low chrome steels by not keeping the oxygen concentration up to a fixed figure by proper aeration?

H. S. RAWDON: That is possible. In the apparatus as we have it now, this variable would be taken care of.

F. N. SPELLER: My impression is that in all of these tests every factor should be kept the same, as far as possible. None of us knows a great deal about corrosion testing. We are now testing methods rather than the materials. The most essential point seems to be to keep all the factors the same throughout the test, and have those factors relatively the same as they are in service. Now, of course, there is a difference of opinion as to how far one can accelerate such tests. Personally, I think it is legitimate to keep the oxygen as high as the temperature and pressure will permit, for it is easier to maintain a state of saturation than to try to keep the oxygen concentration somewhere in between.

Just one other point in regard to these immersion tests. I notice you use the term mg. per sq. cm. per year, and that suggests the question why cannot we agree on a standard unit of corrosion measurement? The standard unit should include (1) the average loss per unit of area per unit of time; (2) the maximum loss per unit of area per unit of time. The latter refers to localization of corrosion or pitting, and this divided by the average loss (both being expressed in centimeters penetration per year) we have termed the *pitting index* or *pitting factor*. These units give at a glance the rate of corrosion and the tendency to pit. The latter varies from 1 upward to 100 or more.

Two measurements are required. One representing the uniformity, which must be determined usually by the loss of weight, and another representing the depth of pitting. These are usually expressed in different units—one, loss in weight, and the other

centimeters or inches penetration, which cannot be compared. Ounces per square foot or milligrams per square centimeter mean little to the average man. The trouble today is that investigators all over the world are using different units, so that their results cannot be readily compared.

W. D. RICHARDSON[14]: I quite agree with what Mr. Speller has said in his last remarks, in regard to the desirability for some sort of unit, which will determine not only the average corrosion upon a surface, but upon the depth of penetration, because it is usually the depth of penetration that determines failure. In other words, your corrosion may be all in one pit, as I have seen it on the bottom of a tank, in one or two very large pits, but the tank had failed. Average corrosion over a surface would tell nothing in a situation like that.

There is a difference in the case of most metals between the action of hydrochloric acid and of nitric acid. To my mind, the secret of corrosion is bound up in the secret of passivity, and until we have a thorough-going investigation of the phenomenon of passivity, we will not be getting to the bottom of corrosion. Now a passive metal, such as iron, dipped in strong, nitric acid, or in chromic acid, is, to all intents and purposes, a noble metal. Iron is a metal which requires the strongest oxidizing acids to induce passivity.

H. A. BEDWORTH[15]: May I make a point in regard to the units for reporting the results of corrosion tests. In all units proposed to date, such as loss in grams per square centimeter per month, or inches penetration per month, one important point is lost sight of. Some mention should be made of the total duration of the tests in order to make results definite, and that results by different investigators may be correlated. In corrosion tests of certain alloys where protective coatings are formed, the rate slows down considerably with the length of duration of test. It is quite evident that results will not be definite unless some mention is made of the length of tests. In carrying out laboratory tests, we must always ask ourselves the question, do these tests show what will happen in actual practice? That is what we want to know. We

[14] Chief Chemist, Swift and Company, Chicago, Ill.
[15] American Brass Co., Waterbury, Conn.

must try to imitate as closely as possible conditions that will be maintained in service. We all recognize the need for accelerated tests, and we should have more data covering the parallelism between service tests and accelerated tests. So far we have very little along these lines.

I would like to add a word in defence of the salt spray test. This test is all right if you use it to test salt spray conditions. Now suppose we want to know what a certain alloy will do for seashore use, what could be better than a salt spray test?

COLIN G. FINK: The intermittent salt solution immersion test.

H. A. BEDWORTH: We also believe that the salt spray test has a direct relation to the corrosion of alloys by sea water, but if one tries to apply those results to other solutions and other conditions, he is in for trouble. The same thing applies to the accelerated electrolytic test. I have serious doubts as to the application of the accelerated electrolytic tests to the general corrosion of alloys. Anderson and Enos have tried to point out the parallelism of the electrolytic test to corrosion in mine waters, and I think there is somewhat more similarity there than would be in a great many other cases, but if those electrolytic tests had been carried out along with the purpose of predicting which alloys would stand up best against mine water, erroneous indications would have been obtained in a number of promising alloys.

The American Society for Testing Materials is carrying out an extensive program with regard to corrosion testing, and is taking first the problem of testing the test. A number of years ago, as anyone who has investigated corrosion literature will find, the matter of corrosion testing was in a chaotic condition, but if we continue to make as much progress along these lines of corrosion testing as we have in the last few years, we shall soon be in a position where we shall know a great deal more than we do at present.

J. R. WITHROW[16]: I would like to emphasize the importance of this intermittent immersion in certain cases, by giving an illustration different from the one mentioned on page 364 regarding sea water and changes of the tide. We have been compelled, in our study of certain chemical engineering materials of construction, to devise and use intermittent immersion testing methods, and it

[16] Prof. of Industrial Chemistry, Ohio State Univ., Columbus, Ohio.

is perfectly obvious that in order to get somewhat close to practical conditions, some such test as that must be used. If you consider a case, for instance, that came to my attention about 18 years ago, where in the distillation of crude acetic acid, which we call raw liquor in the hardwood distillation industry, the copper stills corroded out on the belt around the middle about 6 or 9 inches (15 to 23 cm.) wide. Immediately all sorts of suggestions came forward. If you inspect a kettle where chemical solutions of various kinds are being boiled down, this matter of intermittent drying and wetting of the metal surface is very important. In these cases of chemical engineering materials of construction, the intermittent immersion test is the only one which meets practical conditions, and we, therefore, use this test. In the case of our copper stills, I assumed that air had something to do with the corrosion, on the basis of previous experience with the action of acetic acid on copper in the presence and in the absence of air. I could not determine how air could be in a still which was filled, theoretically at least, with steam or vapor. But I overlooked the fact that the still was being fed continuously from a tank where the material was saturated with oxygen, as far as it could be. Immediately when the cold liquor came into the boiling mass, it probably liberated the oxygen.

Colin G. Fink: What Mr. Withrow says confirms my belief that it is very important to appreciate the value of the intermittent test, such as Dr. Rawdon has described today. Mr. Bedworth takes delight in coming up and vouching for the goodness of the salt spray test. If Mr. Bedworth will take the trouble to use the intermittent test instead of the salt spray test, he will approach actual service conditions much more closely, and will find that certain metals or alloys which stand up remarkably well on the salt spray test fall down rapidly on the intermittent salt solution immersion test.

We have had that point brought to our attention again just recently. It cost one concern a large sum of money, by introducing a metal alloy which stood up remarkably well under the salt spray test, but failed completely in actual service, which closely corresponded to the intermittent salt spray test. I think you will find, if you run parallel tests, regular salt spray versus intermittent

salt spray, or immersing your sample in a sodium chloride solution and allowing it to dry, that you will get quite different results. Of course, in all of these tests, as has been pointed out time and again, we want to approach as closely as possible actual service conditions.

H. S. Rawdon: I might amplify a little what Mr. Bedworth mentioned. He referred to the program that the American Society for Testing Materials has in progress. That society is planning to show the relative merits of various types of corrosion tests, but is not upholding any of these tests as crucial. The salt spray test is to be compared with other types of testing, and the effort will be made to show the advantage of that test in its proper place. I might also correct an impression that Dr. Fink may have given you that the Bureau of Standards discarded this test. We have not discarded it yet, until we get our final results. I do not believe we ever advocated it, however, as a general all-round test. We are still using it on coated metals. A good many people are modifying the salt spray test somewhat, so that it approaches the intermittent immersion test. That is, they allow it to run perhaps for a week and let it dry out thoroughly before starting the spray again.

I thoroughly agree with Mr. Speller in his method of presenting corrosion results where they are applicable. In a case like these results I presented, I do not believe it would have been applicable, because you have not enough corrosive attack, and you do not have any pitting that you can measure with any degree of certainty, as you usually have in a case like a water system where there is pitting and you have an appreciable loss of weight. The method of presentation of corrosion results should take into account the pitting as well as the change in weight.

O. P. Watts[17]: I concur heartily with Mr. Richardson on the importance of studying passivity in corrosion. I have nothing to add in the way of experiments, but should like to express an opinion. In stainless steel I think we are concerned with the passivity of chromium. Aluminum is a metal of high chemical activity, so active that, like sodium, calcium, and magnesium, it cannot be plated out of aqueous solutions, yet we use aluminum cooking dishes. How are we to explain this seeming paradox? Experience in soldering and making electrodeposits on aluminum, and

[17] Prof. of Chemistry, Univ. of Wisconsin, Madison, Wis.

its use in the electrolytic rectifier all point to the presence of a film of some compound, probably the oxide, on the surface of aluminum.

Silicon, like aluminum, shows great chemical activity at high temperatures, and then is a powerful reducing agent; yet massive silicon is very resistant to many corrosive solutions. If a piece of silicon is put into a solution of copper sulfate there is no action; but on adding hydrofluoric acid all the copper is displaced from solution as a coating on the silicon. In the presence of hydrofluoric acid silicon behaves normally, just as we would expect it to do from a knowledge of its reducing power at high temperatures and the large heat of formation of its oxide. The presence of a film of quartz of microscopic thickness would account for the behavior of silicon, just as a film of corundum (Al_2O_3) would explain the abnormal resistance of aluminum to corrosion in many solutions.

Judged by the heat of formation of its compounds, chromium should be among the more active of the heavy metals, but its behavior puts it among the inactive ones. Its oxide, like those of aluminum and silicon, is very resistant to many chemical agents. If we admit that the resistance to corrosion of aluminum and silicon is due to a film of oxide, it is only reasonable to ascribe the remarkable resistance of chromium and high-chromium alloys to the same cause. It requires 12 to 15 per cent of silicon to render iron resistant, as seen in duriron, etc., and it is a curious coincidence that about the same proportion of chromium is necessary to impart stainless properties to steel.

In the long controversy regarding the nature of the passivity of iron, the view most frequently advanced is that of the formation of a film of oxide on the surface of the iron. The term passivity has not been applied to the resistance to corrosion offered by aluminum, silicon and their alloys, because it is a permanent condition of these materials, and not a transitory state like the passivity of iron and nickel; but it is my opinion that in all these cases the resistance is due to a film on the surface of the metal, and hence a further study of passivity is important in advancing our knowledge of corrosion-resisting materials.

C. D. Hocker[18]: This discussion of passivity and resistance to

[18] Research Chemist, Western Electric Co., New York City.

corrosion strikes me as rather reasoning around in a circle. It seems to me that these observations that metal becomes passive when put into certain solutions are merely observations of the fact that the thing is not corrodible in certain solutions, and to say that when we learn more about passivity we will learn more about resistance to corrosion strikes me as another way of saying: When we know more about resistance to corrosion we will know more about resistance to corrosion.

Since it seems to be quite in order in order for one to air his views, while I am talking I might say something about the salt spray test. I agree heartily with Dr. Fink. The salt spray test has been regarded as one more useful than it really is. It is my opinion that there are other ways of evaluating coated metals which are really more discriminating than is the salt spray test. An intermittent immersion test, I agree with Dr. Fink, is better; and it is my opinion that one can get more discriminating results by using, not sodium chloride, but *ammonium chloride* solution in such a test. Neither sodium nor ammonium chloride attacks zinc itself, but ammonium chloride is very effective in dissolving off corrosion products which have resulted by exposure to air, so, by using an ammonium chloride solution one can keep the surface of the article being tested free from corrosion products, and observe better what is going on.

By intermittent immersion of a zinc plated article, allowing it to dry between dips into the solution, one can detect small pin holes which do not appear when the article is kept continuously wet because zinc will protect the article until there is rather a sizable hole in the coating. The test referred to is discriminating enough that it can be used as a tool to indicate whether or not a piece of metal has been cleaned in the proper manner before plating it. If it has not been cleaned properly, slight imperfections in the surface reflect themselves in the continuity of a thin zinc coating.

Also I do not consider the salt spray test to be a desirable method for the testing of nickel coatings. In order to detect thin spots or pin holes in nickel coatings, the most effective way, in my judgment, is to keep the coated article continuously immersed in a test solution of good conductance, because nickel is distinctly electropositive to iron, and as soon as there is a pin hole

in the coating the iron will be made to rust. If one wants to speed up the appearance of rust at pin holes the addition of an oxidizing agent like hydrogen peroxide is helpful.

W. D. RICHARDSON: I wish I could dispose of the question of passivity by a convenient phrase as readily as has Mr. Hocker. Prof. Watts thinks of passivity as due to an oxide film on the surface of the metal, and so do I picture it in that way, and that is a convenient picture to make of it, but there are films and films. We can have a thick visible film, of the nature of Fe_3O_4; we can have an extremely thin film of the same oxide produced by flaming a clean iron surface, but the passive film is very different from this type of film, and we shall no doubt have to get down to molecular dimensions eventually. When we are dealing with metal corrosion in hydrochloric acid or hydrofluoric acid, we are not dealing with passivity phenomena. When we are dealing with a solution of metal in an organic acid we are not dealing with passivity.

G. M. BERRY[19]: In studying this question of passivity of iron, or in studying any particular metal or alloy which develops the property of passivity, we ought to apply the same sort of reasoning that we do in studying equilibria; and then carry that sort of reasoning to the limit of our possible understanding of such conceptions of energy, for instance, as center around the work of Lewis and Langmuir on the relation of electrons in atoms and molecules. When we begin to think of the question of passivity in these terms, are we not then pretty close to the solution of the phenomenon which we define as passivity? If we displace an electron, or change the polarity of an atom or molecule, will it not function in an entirely different way so that it becomes highly possible for the metal surface to show a change, such as is revealed by the passive state?

R. J. MCKAY: It seems to me that the phenomenon of passivity is an interesting factor in corrosion. Ordinarily the co-existence of hydrogen ion and an oxidizing agent will produce rapid corrosion, but in certain cases the presence of a strong oxidizing agent stops corrosion, and we call this passivity. The phenomenon deserves study, but to say that the study of passivity is the only

[19] Chief Chemist, Halcomb Steel Co., Syracuse, N. Y.

thing, or the most important thing, in understanding corrosion is hardly correct.

May I mention Dr. Watts's illustration of cooking utensils, in which he assumed that certain cooking utensils are not corroded. Chemical analysis study of foods, cooked in various cooking utensils, shows that practically all cooking utensils are corroded to a certain extent. It certainly is true that, in general, every food which is cooked in an aluminum utensil will contain appreciable quantities of aluminum. It cannot be assumed that there is a passive condition in this case which entirely prevents corrosion.

H. A. Bedworth: I should have said in connection with my remarks regarding the salt spray test, that the test I referred to was an intermittent test. That throws a considerably different light on the test. The spray was continued during the day and shut down overnight, so that the action was intermittent, and I believe it can be agreed that these conditions very closely approximate seashore conditions, and we believe that they have given the true answer. I have no doubt that they will closely correspond with the intermittent immersion tests. The whole thing resolves itself into a question of—and this applied to any accelerated test—whether it gives the right answer.

R. J. McKay: Regarding salt spray tests and other tests in which the samples are in the atmosphere part of the time, if the metal which is being corroded produces a corrosion product which is hygroscopic, corrosion is accelerated. For instance, if a salt is formed which is hygroscopic at 90 per cent humidity, but not so at 80 per cent humidity, there is comparatively rapid corrosion, because moisture will condense. A change in humidity where the corrosion product is not hygroscopic will make several hundred per cent difference in the rate of corrosion.

Colin G. Fink: If I understand Mr. Bedworth correctly, shutting down the salt spray at night meant that that salt spray test became an intermittent test. But this is not entirely so, because your samples are still exposed to a high humidity at night. If you wanted to make the salt spray test intermittent, Mr. Bedworth, you would have to take your samples out of the box and allow them to dry perfectly. They would not dry if they were kept in the box.

S. J. COLVIN[20]: I believe Mr. Bedworth stated that any test applied to determine corrosion resistance should be a measure of the conditions causing that corrosion. The firm with which I am connected is engaged in the manufacture of automobile rims. Our product is subjected to all kinds of atmospheric corrosion, from that of the salt air along the sea coast to that of the more arid portions of our country. It would seem to me impossible to subject our product to an accelerated test that would embody all types of atmospheric corrosion. We have applied the salt spray test as a continuous test of the corrosion resistance of the zinc coat on our product for about three years. We have attempted to hold the conditions of this test constant over that period, and hope that the salt spray is telling us correctly that we are improving our product when, three years ago, the zinc coating would last about eight hours under this test and at the present time, considerably over forty-eight hours. Do you believe that the intermittent test would be more nearly a measure of the atmospheric corrosion on a rim than would the continuous salt spray test?

COLIN G. FINK: Absolutely, and you get your answer much sooner.

S. J. COLVIN: Of course, the salt spray, as we have it, is in a cabinet, similar to that design recommended by the Bureau of Standards. It is a convenient machine for testing, and it is quite inexpensive. If possible, we do not like to destroy rims to test them, and our salt spray test does not do that. An intermittent type of machine designed to test 15 or 20 rims a day would run into considerable money it would seem to me.

COLIN G. FINK: I shouldn't think so. Would you, Dr. Rawdon?

H. S. RAWDON: I think it would cost considerably more than a salt spray box would. You would have to have rather a husky machine to handle that many rims.

R. J. MCKAY: In discussing the salt spray as a possible test for determining corrosion by the atmosphere, I would like to ask you gentlemen whether your experience agrees with my own regarding

[20] Chief Chemist, Jaxon Steel Prod. Div., Gen. Motors Corp., Jackson, Mich.

the principal agent which causes corrosion in the atmosphere. It is an interesting fact that in studying the corrosion products formed on non-ferrous metal screens, that, samples taken from Hawaii, Central America, Pittsburgh, Texas and New York City contain a higher percentage of sulfates than of any other salt. It is surprising that even samples taken from along the sea coast are in that condition. I would like to ask the gentlemen who have studied the atmospheric corrosion of iron, whether their experience agrees, and if so I would suggest that in an alternate immersion test used to duplicate atmospheric conditions, SO_2 should be contained in the solution.

F. F. Farnsworth[21]: In answer to the question regarding the intermittent immersion testing of automobile rims, the other day I happened to be talking with an investigator who is interested in that particular proposition, and he suggested the possibility of simply mounting the rim on a roller which would slowly turn it letting the lower edge dip into the solution, and then during the rest of the revolution allowing it to dry in the air. In regard to this last question of Mr. McKay's, doesn't the New Jersey Zinc Company already add SO_2 to the intermittent test?

H. S. Rawdon: Yes, but that is for testing zinc coatings only.

[21] Research Chemist, Western Electric Co., New York City.

An address by the Chairman of the Symposium on Industrial Electric Heating, presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 3, 1924.

INTRODUCTION TO SYMPOSIUM ON INDUSTRIAL ELECTRIC HEATING.

By C. F. Hirshfeld.

By way of setting the stage, and arranging the scenery, I should like to make a few remarks about industrial electric heating. We, in Detroit, cannot claim to be the fathers of the industrial electric heating art. It has its roots in many different locations and is scattered well over the industrial world, but we, of Detroit, have done a great deal toward fostering the growth of this particular art, and it is easily explainable when you stop to think of the character of Detroit. You know that youth is always reckless, less conservative than age, and Detroit is industrially a youthful city, although historically an old city. Because of the recklessness of youth I think the art of industrial heating got a start in Detroit on a scale which was larger than in most other industrial centers. Industrial heating is still much of a gamble in many cases, not because it is not amenable to well-known rules and laws, but because so many people get so many queer ideas and try to put these through with inadequate knowledge. Personally, for a number of years past, I have been trying to bring about what you might call education in industrial heating, in order that we might have fewer failures and more successes.

Our program this morning is largely made up of a record of successes.

A paper presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 3, 1924, Prof. Hirshfeld in the Chair.

THE USE OF ELECTRIC FURNACES IN HEAT TREATMENT.[1]

By A. E. White.[2]

Abstract.

The various types of heat-treating furnaces are compared. Examples of performance using various fuels, as well as costs of operation are given. Most of the figures were obtained under actual operating conditions. From the data so obtained, the author is enabled to formulate recommendations for furnace design. The dimensions, heat diffusion, distribution of heating elements, insulation, heat circulation, accuracy of temperature control, resistors and various furnace types are among the factors carefully considered. From all these standpoints as well as from others, the electric heat-treating furnace is found to be advantageous. In comprehensive appendices are given definitions, a table showing heating values for iron at different temperatures, and heat-treatment data from a number of actual plant runs. A very complete classified bibliography is also appended.

[P. D. V. M.]

Recent years have witnessed a most rapid growth in the use of electricity for industrial heating. One large central station, for instance, showed no industrial heating load in 1914, showed a yearly consumption of 30 million kw. hr. in 1918 and a load of 60 million kw. hr. in 1922. It expects a heating load of 110 million kw. hr. in 1924 and a load of 150 million kw. hr. in 1926. No other class of loading for this particular company has shown such a percentage increase. What is true of this company is, or could be, true of most of the other central stations located in industrial communities.

[1] Manuscript received August 6, 1924.

[2] Professor of Metallurgical Engineering and Director of the Department of Engineering Research, at the University of Michigan, Ann Arbor, Mich.

During the war the use of electricity as the source of heat in heat treatment operations spread rapidly. Manufacturers of cannon and shells found that the electric furnace produced a larger percentage of stock, accepted after exacting Government inspection, than did the oil or gas-fired furnace. Since then the automobile manufacturer who must obtain maximum strength with the least weight of metal, and at as low a cost as possible that he may face competition, has also felt the need for better heat-treating furnaces. It is in the automotive industry today that the majority of electrically heated heat-treatment installations may be found.

APPLICATIONS OF ELECTRICAL INDUSTRIAL HEATING.

Electricity for industrial heating has quite diverse applications. It should be thought of as an adjunct in such operations as iron and steel melting, copper, brass and bronze melting; enameling, japanning, glazing; drying for the removal of moisture from material such as food products and wood, welding, and as the source of heat in carburizing, annealing, quenching and drawing operations.

HEAT TREATMENT—ITS NATURE AND EXTENT.

Scientific heat treatment is less than 28 years old. Prior to that period heat treatment operations were performed by rule of thumb methods. It was known that with suitable treatment steel could be softened. It was known that by a suitable heating, followed by an immersion in water or oil, steel could be hardened. It was known that the stiffness and hardness in copper and brass could be removed by a suitable heating. It was known that by packing a low carbon steel in charcoal, and by heating this product for a sufficient time at a suitable temperature, it was possible to convert the soft ductile steel into a stronger, harder product. All of these operations are ones used in heat treatment. The why was not known.

Heat treatment is today an exact science. With a knowledge of cooling curves and constitutional diagrams, the properties obtainable in metals after heat treatment can be predicted with considerable accuracy. Further, to produce given physical properties, one can state with certainty, for many of our metals and alloys, the temperatures which should be employed and the rate of cool-

ing which should be used. Yet, in spite of our present knowledge, we have much to learn. Constitutional diagrams have not been prepared for all of our alloys. Constitutional diagrams are mainly useful for binary alloys. With three elements only a few workable constitutional diagrams have been prepared. With four or more elements it is not possible to prepare a constitutional diagram.

No exact figures as to the quantities of metal heat treated are available. In the ferrous field alone it is safe to state that at least two million of the thirty-five million tons of steel produced last year were heat treated. Most forgings and castings are heat treated. All tool steel is heat treated. Definitions for some of the heat-treatment terms used will be found in Appendix A. Many of the important parts in automobiles and in railroad locomotives are heat treated.

In one of the higher-priced automobiles over eighty-four of the important parts receive heat treatment. Many of these parts receive more than one heat treatment. For instance, in the case of a transmission countershaft, initially a low-carbon alloy steel, the following heat treatments are given: a heating to 1,550° F. (843° C.) for two hours, followed by a water quenching; a heating to 1,200° F. (649° C.) for two hours followed by an air cooling; a carburizing operation carried out at a temperature of 1,700° F. (927° C.) for eleven hours, followed by an air cooling; a heating to 1,550° F. (843° C.) for twenty minutes, followed by an oil quenching; a heating to 1,400° F. (760° C.) for twenty minutes, followed by an oil quenching, and finally a heating to 1,250° F. (677° C.) for five minutes, followed by a water quenching.

The purpose of these various operations is to produce a steel of exceptional hardness on the outside and of maximum ductility on the inside. The first two operations are performed in order to place the steel in a proper condition for machining and carburizing. The carburizing operation is for the purpose of introducing a high percentage of carbon into the outer zone of the steel. The treatments following the carburizing operation are for the purpose of producing a fine compact grain or crystal structure in both the core and the case; with the further purpose of getting the case or outer zone in a condition of maximum

toughness and hardness, and the core or inner zone in a condition of maximum toughness.

When one realizes that steel is apt to warp when quickly heated or when suddenly cooled, and when one further realizes that in the heat-treatment operations given to gears it is necessary to hold many of them to within 0.003 of an inch (0.076 mm.) on the flat and to within 0.004 of an inch (0.102 mm.) on the round. one can realize some of the difficulties which continuously face the successful heat treater.

THE HEAT-TREATMENT FURNACE.

There are no factors which assist the heat treater to a greater degree than good furnace construction and automatic operation and control. Therefore, to just the extent that furnace construction is sound, and furnace operation is made automatic, will the problem of the heat treater be lessened. The most important tool in the hand of the heat treater is his furnace. It is a tool which until recently has received little consideration. It will be the purpose of this paper, therefore, to discuss furnaces, especially electric furnaces, and the part they play in heat treatment.

In the various conferences which have been held with individuals relative to the respective merits of oil, gas and electrically heated furnaces, a considerable number of the persons interviewed have been outstandingly in favor of electric heating. A representative of one of the largest automobile companies has stated that at the first possible opportunity his company will carry out all of its heat treatment in electrically heated furnaces. This same statement was made by representatives of many of the other companies interviewed. Some of the outstanding reasons for such statements are as follows:

1. An even temperature.
2. Accurate automatic temperature control.
3. Freedom from gases, with elimination of excess scaling and pitting.
4. Heating by uniform radiation, rather than by cyclonic blasts of gases.
5. More comfortable working conditions.
6. More uniform product.
7. Fewer retreatments.
8. Less scrap.
9. Ability to locate furnaces in closer relation to preceding or succeeding operations.

Not the least of these reasons is the material reduction in scrap and retreatment. A representative of one of the largest plants in Detroit, combining together the scrap and retreatment losses, states that the loss in oil furnaces is 18 per cent, in producer gas fired furnaces 15 per cent and in electric furnaces is 0 per cent.

A representative of another large automobile plant states that the retreatment and scrap losses for the transmission gears at his plant are 12 per cent retreatment and 3 per cent scrap for the gears heated in oil-fired furnaces, as compared with 4 per cent retreatment and 2 per cent scrap for the gears heated in electric furnaces. This latter statement represents without doubt a more general experience, as it is difficult to imagine a retreatment plus scrap loss of 0 per cent in spite of the excellent control.

TYPES OF HEAT-TREATING FURNACES.

Most heat-treating furnaces are used for the heating of iron and steel. These are known as forging, carburizing, annealing, quenching and drawing furnaces. In the non-ferrous field large numbers of furnaces are used for heating the metal preparatory to shaping and for annealing.

Forging Furnaces.

Most forging furnaces use oil as the heat-producing medium. Most of these furnaces have only one burner. The hearth area is usually small, frequently not exceeding 30 in. (763 mm.) in width, 30 in. (763 mm.) in depth and 8 in. (202 mm.) in height. These furnaces are so operated as to bring the stock to the desired temperature in the minimum time. No appreciable consideration is given to furnace efficiency. Operators of forging departments will advise that considerable precautions are taken to prevent the metal from becoming burnt. The frequency with which injured metal is found in succeeding operations, however, indicates that the art of heating metal for forging purposes has not as yet been surrounded with adequate safeguards.

A number of attempts have been made to design electrically heated forging furnaces. There are none to date which are successful. All of the metallic resistor furnaces designed for this purpose have failed because of the inability of the resistor to stand up successfully under furnace temperatures in excess of

1,800° F. (982° C.). There is need for a heating resistor that will successfully produce temperatures between 1,800° and 3,000° F. (982° and 1,649° C.). Several resistors have been advanced for this particular service. None of them, however, at this writing, appears to meet exactly the requirements. A number of companies are devoting considerable attention to the development of electrically heated forging furnaces. It is hoped that some one of these attempts will be successful, because there is a strong demand, even at this time, for furnaces in this field.

TABLE I.

Fuel Costs of Carburizing in Oil-Fired Furnaces.

	Cam Shaft Box	Small Box
Gross weight	385 lb. (175 kg.)	110 lb. (50 kg.)
Weight of parts	126 lb. (57 kg.)	24 lb. (10.9 kg.)
Hr. coming up to heat	4	2
Fuel hr. coming to heat	10.8 gal. (40.9 L.)	8.6 gal. (32.5 L.)
Total fuel coming to heat	43.2 gal. (163.7 L.)	17.2 gal. (65.1 L.)
Hr. holding heat	19	13
Fuel hr. holding heat	5.8	4.6
Total fuel holding heat	110.2 gal. (418 L.)	59.8 gal. (227 L.)
Total fuel; whole heat	153.4 gal. 582 L.)	77.0 gal. (292 L.)
Gross load	4620 lb. (2099 kg.)	3520 lb. (1600 kg.)
Net load	1512 lb. 688 kg.)	768 lb. (348 kg.)
Fuel used, gross load	0.0332 gal./lb. (0.278 L./kg.)	.0219 gal./lb. (0.183 L./kg.)
Gross load efficiency	5.90 per cent	10.25 per cent
Fuel used, net load	0.1014 gal./lb. (0.838 L./kg.)	.1003 gal./lb. 0.839 L./kg.)
Net load efficiency	2.25 per cent	2.29 per cent
Fuel cost, gross load	$0.00212/lb. ($0.00467/kg.)	$0.00140/lb. ($0.00309/kg.)
Fuel cost, net load	$0.00650/lb. ($0.01435/kg.)	$0.00642/lb. (0.01416/kg.)
Cost of oil at burner	$0.064/gal. ($0.0169/L.)	

Assumed 130,000 B.t.u./gal. (8,680,000 cal./L.)

NOTE.—Gross efficiency is determined by dividing the heat required to heat the carburizing box, the carburizer and the stock, by the heat actually used. Net efficiency is determined by dividing the heat necessary for the stock by the heat actually used.

Furnaces for Carburizing.

Furnaces for carburizing are of two main types. One is of such design that the work to be carburized is packed into boxes of either steel or a special alloy with the carburizing compound. This box and its contents are brought up to the desired heat. This heat lies between 1,650° and 1,750° F. (899° and 954° C.).

It is maintained at from 4 to 20 hours, depending upon the depth of the case desired. The other type of carburizing furnace is one in which most of the carbon for the case is obtained from the carbon monoxide contained in city gas.

Most of the furnaces of either type are fired with gas or oil. Oil is the predominating fuel. Strange as it may seem, practically no companies engaged in carburization keep daily cost records. Individual tests have been made from time to time, and as a result of these tests one is reasonably safe in stating that the efficiency of oil-fired carburizing furnaces, expressed in gross load, is between 5 and 10 per cent. The exact figure for one particular test was 6.9 per cent and for another test 10.25 per cent. The net efficiency probably lies between 2 and 2.5 per cent. The exact efficiency in one test was 2.25 per cent and in another test was 2.29 per cent.

One of the very few oil-fired carburizing cost records which has come to the writer's attention is given in Table I. These data were taken from one of the large automobile plants in Detroit.

At a time when new installations or changes in installations are proposed, it is customary to estimate savings to be expected as a result of the change. Frequently these analyses do not set forth furnace efficiency. As an example of this type of cost data the following analysis on carburizing rollers is submitted:

TABLE II.

Box versus Gas Furnace Costs for Carburizing Rollers.

Number of rollers used on 300 jobs		47,100
Pound rollers used on 300 jobs		1,442
Boxes required		77
Carbon compound cost per day at 3.5c lb. (7.2c kg.)	Oil-fired furnace	$10.03
	Gas-fired furnace	10.07
Cost of gas at 60c per 1,000 cu. ft. (2.12c per cubic meter), gas-fired furnace		4.21
Cost of oil at 6c per gal. (1.58c per L.), oil-fired furnace		26.46
Cost of packing with oil-fired furnace		16.85
Saving on 300 jobs by using gas		39.10

The fuel cost in the oil installation was $26.46 as compared with $4.21 for gas.

An examination of these data would indicate the absence of furnace efficiency. Sufficient data is submitted, however, to enable its determination. On the assumption that the carburi-

zation is done at 1,700° F. (927° C.) the gas-fired furnace shows a net efficiency of 10.4 per cent, and the oil-fired furnace shows a net efficiency of only 0.7 per cent. This is an extremely low efficiency record, although many carburizing furnaces doubtless operate with as low a value.

There are very few carburizing furnaces of the continuous type. In plants engaged in quantity carburization, the continuous type possesses definite advantages over the stationary type.

In one of the most recent as well as almost the only installation of the continuous oil-fired type, the carburizing boxes pass through the furnace on rails placed at a downward slope of about 30°. The boxes are assisted in their downward travel by pusher mechanism. No records were available from this installation with regard to operating efficiency. The stock treated in these furnaces had a very uniform case.

At this writing there are authentic data on only two electrically heated carburizing furnaces in operation in this country. These furnaces are engaged in the carburization of miscellaneous automobile parts. They are of the annular ring or doughnut type construction. They have proven satisfactory both with respect to the quality of the work which they perform, and with respect to operating costs. In this latter connection the following data with reference to these furnaces for the month of April, 1924, may be of interest.

Total number of boxes	26,161
Gross number of boxes and stock in pounds	3,270,125 (11,486,420 kg.)
Net weight of stock in pounds	650,877 (295,853 kg.)
Total kw.-hr. consumed	329,567
Average cost per kw-hr	$0.0134
Total power cost	$4,426.10
Pounds of gross stock per kw-hr	9.95 (4.52 kg.)
Gross load efficiency (cold stock at 25° C.)	86.6 per cent
Pounds of net stock per kw-hr	1.97 (0.897 kg.)
Net load efficiency	17.4 per cent.
Cost of power per lb. of gross stock	$0.00135 (0.00289 per kg.)
Cost of power per lb. of net stock	$0.0068 (0.0149 per kg.)

A careful analysis of the cost of heat expressed in terms of pounds of net product with this furnace installation, and with the average oil-fired installation, shows but little difference. The reason is not due to the fact that electricity as such, per B. t. u. (cal.) value, is cheaper than oil. The reason is due to the fact

that in the electric furnace installations just mentioned an excellent operating efficiency is obtained. For instance, the electric furnace operated with a gross efficiency of 86.6 per cent. and a net efficiency of 17.4 per cent. Oil-fired carburizing furnaces, on the other hand, seldom, if ever, exceed a gross efficiency of 10 per cent and a net efficiency of 2.5 per cent.

Furnaces for Annealing.

Most annealing furnaces are of the box-type construction. A large percentage of them are oil fired. Many of them are so designed that they can be used in heating for quenching or in heating for drawing, as well as for straight annealing. A number of the larger-sized furnaces are of car-type construction. This design is employed to a considerable degree for furnaces used in the heat treatment of steel castings.

No figures have been obtained with reference to the efficiencies of the furnaces engaged in annealing. We have data showing the efficiencies of electrically heated furnaces engaged in heating for quenching and we have one efficiency record for a water gas furnace engaged in heating for the same purpose. These efficiencies, however, should correspond to the furnace efficiencies in annealing. In an article by E. F. Collins,[3] figures are given for the efficiency of a direct oil-fired and an electrically heated furnace. These follow: 16 per cent for the oil-fired furnace and 80 per cent for the electrically heated furnace. Hansen[4] checks these figures quite closely, as he gives electric furnace efficiency at 87 per cent and oil-fired furnace efficiency as 15 per cent.

It is the opinion of the writer that these figures give a fair picture of conditions as they exist in general operation today. In support of this statement we have figures showing an efficiency of from 30 to 31 per cent for a furnace using water gas, engaged in heating for quenching, and efficiency records of 48.3, 59.6, 82, 77, 85 and 86 per cent for electrically heated furnaces engaged in heating for quenching.

The Snead electric method for annealing represents a recent development. It is mainly applicable on stock of the same cross

[3] E. F. Collins, Electrical Energy Economical for Heat Treating, Trans. Am. Soc. for Steel Treating, 5, 67 (1924).

[4] F. A. Hansen, Electric Heating Applied to the Steel Industry, Assoc. Iron and Steel Elec. Eng., 4, 765-776 (1922).

section. It consists in passing an electric current through stock, and because of the heat developed as a result of the resistance which the stock offers to the passage of the electric current the stock becomes annealed. Two plants engaged in the manufacture of brass condenser tubes use this method of annealing. It requires an individual operation for each piece of metal. Less than a minute is needed for each anneal. At least one of the plants using this method advises that it can anneal stock as rapidly and at as low a labor charge as when they employ the common batch method for annealing. Unusual control is obtained by this treatment. The stock can be so treated that each of the pieces has substantially the same degree of temper. Also wonderful uniformity in grain size is obtained. It is a method which will doubtless be used on stock of uniform cross section to a constantly increasing extent, in order that producers may better meet the properly exacting requirements of the consumers.

Furnaces for Quenching and Drawing.

Furnaces employed for quenching and drawing will be discussed under the same heading, for the reason that it is common practice to use furnaces engaged in heating for quenching, interchangeably with furnaces engaged in heating for drawing. The only change required when one converts a drawing furnace into a quenching furnace, or a quenching furnace into a drawing furnace, is a change of the temperature in the furnace. Most quenching furnaces operate at temperatures of from 1,380° to 1,550° F. (750° to 843° C.) and most drawing furnaces operate at temperatures of from 600° to 1,200° F. (316° to 649° C.) with an appreciable portion of the drawing temperatures at from 1,000° to 1,200° F. (538° to 649° C.). Most of these furnaces are of box-type construction. A large proportion of them are oil fired.

The electric furnace is making rapid inroads into this particular field. The general designs of the electric furnaces employed are, (1) box-type construction, (2) reverse-flow construction, (3) annular-ring or doughnut-type construction. Though we have only a few furnaces of the reverse-flow type, the general principle is one which seems to appeal to persons giving thought and consideration to economy of operation in heat treatment. They are rapidly finding favor. The doughnut type of construction

is also admirable, inasmuch as it permits of continuous operation with very little heat loss.

The efficiencies of the oil-fired furnaces are probably seldom above 16 per cent. Were efficiencies taken from a large percentage of the oil-fired furnaces, it is probable that most of the efficiencies would lie between 5 and 10 per cent. Unfortunately, this statement is not supported with actual test records. It is made, however, after a careful study of the usual conditions under which oil-fired furnaces are operated, and it is believed to be both conservative and correct.

The efficiencies of the various electrically heated furnaces range from 48 per cent as a minimum to a value of nearly 150 per cent as a maximum. The latter figure, namely, 150 per cent, was given by a representative of one of the large automobile manufacturers in Detroit. It related to a furnace of the reverse-flow type which has only been recently installed. This apparent over-efficiency results from the heating of the incoming stock by the heat transfer from the outgoing stock. This same representative gave furnace efficiencies for four other installations of from 85 to 86 per cent. One furnace showed an efficiency of 85 per cent and three 86 per cent.

The efficiencies of the three electrically heated units of the doughnut-type construction showed respective values of 48, 59 and 77 per cent. The two lower efficiencies are doubtless due to operation at under-capacity. This statement is supported by the fact that one of them operated at 77 per cent efficiency, and carburizing furnaces of the same type operated throughout an entire month at a gross efficiency of 86.6 per cent.

Hump Furnaces.

Hump furnaces derive their name from the characteristics of the permanent pyrometer record. A properly charged furnace during the heating operation shows a hump when the critical point of the steel is reached. The operator is thus enabled to know when the stock has reached a suitable temperature for quenching. The need for a sharp detection of the critical point, especially in gear stock, is great. A temperature rise above the critical of only 50° F. (28° C.) may be sufficient to result, when the stock is quenched, in it becoming excessively warped. Such warp-

age results in undue expense for straightening or even, in some cases, in the complete scrapping of the stock. The furnaces are usually of small capacity. They are seldom over 16 in. (406 mm.) deep and 24 in. (610 mm.) in diameter. They are all electrically heated. As a rule, they operate with excellent efficiency. One figure given is 58.6 per cent. From data which were procured at a recent test at one of the large automobile plants, efficiencies of 38.7 and 43.1 per cent were obtained with these furnaces when the stock was charged into a cold furnace. An efficiency of approximately 85 per cent was obtained when the stock was charged into a hot furnace. This represents usual practice. The exact records of these tests are given in Table III.

TABLE III.

Hump Furnace Data on Steel for Quenching.

Operations	Time A. M.	Meter Reading	Kw.	Temp. ° F.	Temp. ° C.	Effic. Per cent
Test No. 1. Differential Gear. Wt. 91 lb. (41.3 kg.)						
Start charging	7.43	0000.9	..	100	37.8	....
Finish charging	7.44	0000.9	..	100	37.8	....
At heat	9.41	0002.4	15	1390	743	....
Start unloading	10.00	0002.5	1	1400	760	....
Finish unloading	10.01	0002.5	..	1380	737	38.7
Test No. 2. Motor Crankshaft Sprocket. Wt. 109 lb. (49.6 kg.)						
Start charging	10.01	0002.5	..	1380	737	....
Finish charging.....	10.02	0002.5	..	1200	649	....
At heat.....	11.18	0003.3	8	1425	774	....
Start unloading.....	11.40	0003.4	1	1425	774	....
Finish unloading.....	11.41	0003.4	..	1420	771	84.3
Test No. 3. Motor Crankshaft Sprocket. Wt. 124 lb. (56.4 kg.)						
Start charging	7.13	0005.0	..	450	232	....
Finish charging.....	7.14	0005.0	..	450	232	....
At heat.....	9.56	0006.8	18	1425	774	....
Start unloading.....	10.22	0007.0	2	1425	774	....
Finish unloading.....	10.23	0007.0	..	1415	768	43.1

Most automobile plants are today equipped with a considerable number of these furnaces. In fact, almost all of the gears used in automobiles are heated for quenching and drawing in furnaces of this type. In one of the Detroit plants the number of large and small-sized hump furnaces totals 84.

Cyaniding Furnaces.

Cyaniding consists in immersing steel in liquid potassium or sodium cyanide when at about 1,575° F. (857° C.). The steel thus immersed becomes thinly carburized, so that when it is properly quenched it possesses an extremely hard shell from 0.001 to 0.002 in. in thickness. Attempts have been made to heat these pots with electricity, but so far without success. One of the main difficulties is due to the fact that during cyaniding the salt is slopped over onto the resistor ribbon by the furnace operator with a resultant unduly rapid deterioration in the heating coils.

Saltpeter and Oil Drawing Furnaces.

Saltpeter and oil drawing furnaces, as well as Babbitt melting furnaces, present possibilities for the application of electric heat. For the most part, however, these furnaces are today operated with city gas.

LACK OF COST DATA FOR HEAT TREATMENT.

As visits were made to various plants for the purpose of gathering heat-treatment data, it was noted with regret that little attention was given to the maintenance of suitable cost records. It is possible that a careful analysis of the whole situation indicates that the maintenance of careful cost records was inadvisable. That is, that the possible savings through the maintenance of cost records would not equal the cost involved in procuring such records. It is hard to imagine that this condition exists, although it is quite possible that this is the reason why more accurate cost data are not available. Most of the oil-fired furnaces are arranged in batteries, with oil fed to all of the furnaces from one central source. Most plants have no means for measuring the amount of oil used at any one individual furnace. The same general situation is true with the gas-fired furnaces. Whatever cost data are obtained is usually for the purpose of ascertaining the respective merits of one type of furnace over and above another type. Such cost data are of value for the most part only for the moment. They do not give any indication with regard to production costs over a given period of time under plant operating conditions.

GENERAL RECOMMENDATIONS FOR FURNACE DESIGN.

As a result of the study made, a list of certain essentials for suitable furnace design is submitted.

1. Length.

For furnaces of box-type construction the question of length should be carefully considered. One should keep in mind that the furnace length should not be so great as to produce in a furnace requiring uniform heat, considerable temperature difference at various sections along the length. This statement does not apply to furnaces of the counter-flow design, nor, of course, to furnaces of the rotary or doughnut type of construction.

2. Hearth Cross Section.

The width and height of the hearth of all furnaces should be the least practicable. The wider the hearth the greater the temperature difference. In electrically heated furnaces, with heating elements on both sides of the hearth, it is possible to construct a furnace with a hearth five feet in width without injurious results. With oil-fired or gas-fired furnaces, with burners on one side only, hearth width should not exceed three feet.

Hearth height is a matter of considerable importance. It should probably lie between 6 and 36 in. (152 and 914 mm.). With electric furnaces, with the heating element on the side, considerable height will be necessary in order to obtain a proper length of resistor. With the heating element on the sides and underneath, however, the hearth height can be considerably reduced.

3. Heat Difference.

So far as is practicable, it is desirable to keep the temperature at the heat source within 200° F. (93° C.) of the maximum heat desired for the stock. In some cases the temperature difference between the heat source and the heat in the stock should not exceed 100° F. (37.8° C.) during the whole heating cycle. This later arrangement is possible in electric furnaces, although the difference first mentioned is the one usually employed.

Electric furnaces are inherently superior to oil- or gas-fired furnaces in this respect. The temperature just beyond the nozzle of the oil-fired burners usually ranges from 3,000° to 3,500° F. (1,649° to 1,927° C.). It reaches this temperature even when it is not desired in any case to heat the stock above 1,500° F. (816° C.). In place, therefore, of a temperature difference of 200° F. (93° C.), we have a difference of from 1,500° to 2,000° F. (816° to 1,093° C.). This temperature difference results in rapid deterioration of the carburizing boxes used in carburization, and tends to produce overheating of stock in the annealing, quenching and drawing operations. It is also very injurious to the refractories in the furnaces.

4. *Uniform Distribution of Heating Elements.*

Heating units should be placed uniformly around the furnace. This is common practice for electrically heated furnaces. This is done to some extent in gas-fired furnaces. The tendency for oil-fired furnaces, however, is to heat them only with one burner. This principle is totally wrong from the standpoint of obtaining in the furnace at all sections, uniform heat distribution.

5. *Suitable Furnace Insulation.*

Practically all heat-treatment furnaces should be suitably insulated. They should be so insulated that the temperature at the outside of the supporting plates does not exceed 110° F. (43° C.). One of our automobile manufacturers requires all of his heat-treatment furnaces to be lined with at least 4.5 in. (114.3 mm.) of firebrick and with at least 12 in. (304.8 mm.) of silocel, infusorial earth or a similar heat-insulating substance. This manufacturer insists that the furnace walls shall be properly riveted and supported with plate at least 0.25 in. (6.4 mm.) thick. He also stated that if the builders of oil- and gas-fired furnaces followed these practices the initial furnace costs for these types of installations would be considerably higher than is today the case. He further stated that he believed that, when properly insulated, the construction costs for oil- and gas-fired furnaces would be substantially the same as for electrically heated furnaces.

6. Suitable Heat Circulation within Furnace

Furnaces should be so designed as to permit suitable heat circulation within the furnace. In any case, furnaces with solid hearths should be equipped with supports to permit heat underneath as well as on the sides and on the top of the work. Where possible the hearth should be of such design as to permit circulation of heat underneath it. In fact, supports should be used, even in conjunction with the hearths which are of such construction as to permit heat circulation beneath.

7. Freedom from Obnoxious Gases and Fumes.

Furnaces should be so designed as to provide maximum freedom from obnoxious gases and fumes. Gases of this type are commonly found in oil-fired and gas-fired furnaces. They are seldom, if ever, found in electrically heated furnaces.

8. Freedom from Excessive Radiating Temperatures.

This matter was touched upon when it was suggested that the temperature at the outside of the furnace should in no case exceed 110° F. (43° C.). With a furnace insulated so as to operate under this condition, the workmen would have no more objection to working around the furnace in summer than they would have to operating a lathe. In fact, in one of our large automobile plants using both electrically heated and oil-fired furnaces, the workmen operating the oil-fired furnaces have at times been insistent in their demands to operate, at least alternately, the electrically heated furnaces.

9. Accurate Temperature Control.

The main essential for all heating operations is to reach a given temperature. In most designs this temperature should be the same in all parts of the furnace. In some of our earlier furnaces a temperature difference of at least 200° F. (93° C.) was found. That heating means, therefore, which provides the most uniform temperature, is the means which should be most favorably considered. Electrically heated furnaces are of this type. Likewise

furnace temperatures where possible should be automatically controlled. Satisfactory automatic control has been developed for gas-fired and electrically heated furnaces. We have automatic control for oil-fired furnaces. The control itself is satisfactory, but the nature and character of the oil, namely its viscosity, prevents the control from always functioning in a satisfactory manner.

10. Types of Furnaces.

Electric furnaces may be divided into the following types:

(*a*) *Box Type.* This furnace is a design which is admirably suited for many types of work. Its operation, naturally because of its design, is intermittent.

(*b*) *Pusher Type.* Furnaces of this type are acceptable for the treatment of uniform stock. They are being used with excellent success on connecting rods, gears and parts of a similar character.

(*c*) *Conveyor Furnaces.* These furnaces are not always successful, owing to the rapid deterioration of the conveyor, plus the normal tendency of the metal in the conveyor to expand when subjected to the heat in the furnace.

(*d*) *Car Type.* These furnaces are satisfactory from the operating standpoint of getting stock into and out of the furnace quickly. Their efficiency is not overly high, because of the fact that the heat contained in the hearth is lost as the car is removed from the furnace.

(*e*) *Annular Ring or Doughnut Type.* This is a type of furnace which is quite successful. It is a type quite frequently employed by electric-furnace designers. The annular ring, on which the stock is placed, rotates and thus permits easy loading and unloading.

(*f*) *Counter Flow Type.* This is a type of furnace which lends itself to work which can be heated in a continuous furnace. It is a type which is only beginning to come into the field. Its construction is such that it cannot be used in heating for quenching, but it can be used in heating for annealing, drawing or car-

burizing, if it is desired to cool the stock in the carburizing box slowly. Its principle for these operations is excellent, because much of the residual heat in the stock which has already passed through the zone of maximum heat, is absorbed by the stock moving in the opposite direction and just preceding the time when it enters the zone of maximum heat.

(*g*) *Muffle Furnaces.* There are a number of muffle or semi-muffle furnaces on the market. The purpose of the muffle, naturally, is to prevent the products of combustion, or the gases within the furnace, from coming in contact with the work. No really successful high-temperature furnace of this type has as yet been developed. Owing to the limitations of the refractories, muffles possessing satisfactory life have not yet been built. Likewise, many of our non-metallic muffles develop considerable gaseous porosity when heated, and therefore the muffle itself serves merely to protect the work from direct flame and impingement, rather than from contact with the gases within the furnace. The temperature control in these furnaces is also sluggish.

11. Resistors.

In electric furnaces the resistors should receive careful consideration and attention. A few years ago there was a tendency to make them too thin. The result was that they were worn out rather rapidly. Today they are commonly made of metal 0.375 in. (9.5 mm.) in thickness. As an auxiliary to the resistor is the resistor support. A careful study has been given to their designs and to the materials of which they should be made. The failure to satisfactorily meet both of these factors in the early days of the metallic resistor-type furnaces, resulted in short resistor life. From recent observations it would appear that these objectionable features have been removed, so that one should find no difficulty in obtaining for these resistors and their supports, a life, with a properly designed and operated furnace, of from four to five years, or much longer, provided a reasonably low value of current density is taken.

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APPENDIX A.

Definition of Heat Treatment Terms.

Heat treatment refers to such operations as carburizing, annealing, normalizing, quenching and drawing. There are countless definitions for each of these operations.

By carburizing is meant the operation by which carbon is introduced into the outer surface of steel while in a solid state by a long continued heating at a suitable temperature—a temperature, for example, of 1,700° F. (927° C.).

By annealing is implied the operation of heating steel to a temperature above its critical temperature, and following this operation by a slow cooling. The critical temperatures for various classes of steel vary, although they usually lie between 1,400° and 1,500° F. (760° and 816° C.).

Normalizing is an operation similar to annealing, except that the steel is subjected to an air cooling in place of a slow cooling.

Quenching is an operation which consists in heating steel above its critical temperature, and following this with an immersion when at such a temperature in some suitable liquid, such as water or oil.

Drawing is an operation which consists in removing the strains set up by quenching. It is carried out by heating the steel to some suitable temperature below its critical temperature, namely, such temperatures as lie between 600° to 1,200° F. (316° to 649° C.), and following this with a suitable cooling, either slowly or in air or in some suitable liquid, such as water or oil.

APPENDIX B.

Table IV.

Table of Heating Values for Iron

Temperature		Mean Specific Heat	Heat Absorbed Calories	Heat of Recalescence Calories	Total B.t.u./lb.	Total cal./kg.
° F.	° C.					
32	0					
100	38	0.11113	4.22	...	7.58	4.22
200	93	0.11392	10.59	...	19.05	10.59
300	149	0.11506	17.17	...	30.85	17.17
400	204	0.11741	23.94	...	43.05	23.94
500	260	0.12033	31.23	...	56.35	31.25
600	315	0.12345	38.85	...	70.00	38.85
700	371	0.12698	47.18	...	85.00	47.18
800	426	0.13076	55.66	...	102.00	55.66
900	482	0.13547	65.20	...	117.30	65.20
1000	538	0.13956	75.00	...	135.00	75.00
1100	594	0.14435	85.70	...	154.20	85.70
1200	639	0.14852	95.00	...	171.10	95.00
1300	705	0.15877	111.80	5.3	211.00	117.10
1400	760	0.16670	126.70	5.3	237.80	132.00
1500	816	0.17030	139.00	5.3	259.40	144.30
1600	871	0.17320	151.10	5.3	281.90	156.40
1700	926	0.17590	162.90	5.3	302.40	168.20
1800	982	0.17830	175.00	5.3	324.50	180.30
1900	1038	0.17833	185.00	5.3 + 6 = 11.3	353.00	196.30
2000	1095	0.17747	194.20	11.3	369.80	205.50

The values for the mean specific heats for iron were determined according to the method given in "Metallurgical Calculations," by Jos. W. Richards, Part I, page 67.

I. Sm (0 to t) (t up to 660° C.) $= 0.11012 + 0.000025\ t + 0.0000000547\ t^2$
Heat of recalescence = 5.3 cal. absorbed from 660° to 720°.

II. Sm (0 to t) (t = 720° to 1000° C.) $= 0.218 - 39/t$
Heat of recalescence = 6.0 cal. absorbed between 1000° and 1050° C.

III. Sm (0 to t) (t = 1050° to 1160° C.) $= 0.19887 - 23.44/t$
Sm = mean specific heat; t = temperature in °C.

The values given in the table were obtained by the use of the above formulæ. The total heat expressed in calories per kilogram is obtained by multiplying the mean specific heat by the temperature difference. The lower temperature for the values given in the table is 0° C. The values expressed in calories per kilogram

have been converted into British thermal units per pound by multiplying by the factor 1.8.

In determining the efficiencies given in the paper it has been assumed that the temperature of the cold stock was 25° C. With such an assumption and with a deduction of 3 cal. per kg., or 5 B. t. u. per pound, it has been possible, through the use of this table, to determine efficiencies directly. For instance, if stock were to be heated to 1,000° F. (538° C.), it would have a B. t. u. value per pound of 135 were the temperature difference 968° F. (538° C.) (1,000° F.–32° F.). Since the temperature of the stock is assumed to be 77° F. (25° C.) then the B. t. u.'s required per pound would be 135–5 or 130.

NOTE. The value for 705° C. is the mean value of the values determined by formulæ 1 and 2. The value for 1038° C. is the mean value for the values determined by formulæ 2 and 3.

APPENDIX C.

Heat-treatment furnace data obtained from a number of plants visited are submitted on the following pages. Visits were made to representative plants employing electric furnaces in heat treatment operations. Such data as possible with respect to these furnaces were obtained at these plants. In addition data were obtained at most of these plants with respect to their oil-fired and gas-fired heat-treating furnaces. It is believed that all of the data are reasonably representative of that which it would be possible to obtain at most other plants using furnaces for heat treatment operations, whether they be oil-fired, gas-fired or electrically heated.

Table V.

Specifications for Heat Treating Furnaces.

Maker	Inside Dimensions						Fuel	Heating Elements		Hearth
	Length		Width		Height			Sides	Bottom	
	In.	Cm.	In.	Cm.	In.	Cm.				
Stewart‡	15	38.1	10	25.4	5	12.7	Gas	Stewart	4	Solid Br.
	15	38.1	8	20.3	8	20.3	Gas	2 on each side		Sol.
Tate-Jones‡	14	35.6	10	25.4	6	15.2	Gas	Tate-Jones	2	Carbo.
	20	50.8	15	38.1	8	20.3	Gas			Br.
	20	50.8	15	38.1	8	20.3	Gas			
Std. Fuel & Eng.‡	12	30.5	6	15.2	8	20.3	Gas	Std. F. & E. 2 on each side	4	Solid Br.
Bellevue‡	30	70.6	22	55.9	7	17.8	Gas	Bellevue	1	Solid Br.
	30	70.6	22	55.9	7	17.8	Gas			
Tate-Jones*‡	20	50.8	10	25.4	7	17.8	Gas	Tate-Jones	1	....
†	300	767	48	121.9	36	91.4	Oil	7 per side	..	Solid
§	84	213.4	48	121.9	36	91.4	Oil	1 in front	..	....
§	84	213.4	48	121.9	36	91.4	Oil	1 in front	..	Solid
§	108	274.3	60	152.4	48	121.9	Oil	2 on same side	..	Car type
§	15	38.1	12	30.5	30	76.2	Oil	1 only on side	..	....
‡	20	50.8	10	25.4	7	17.8	Gas	1 at end	..	....
	Diameter									
	In.		Cm.							
Stewart*‡	9		22.9		9	22.9	Gas	Stewart	1	Solid
Tate-Jones*‡	10		25.4		12	55.9	Gas	Tate-Jones	1	....
Stewart*‡	11		27.9		9	22.9	Gas	Stewart	1	....
Stewart*‡	15		38.1		9	22.9	Gas	Stewart	1	....
Continental*‡	15		38.1		9	22.9	Gas	Anthony	1	....

* Pot Furnace.
† Pusher Furnace.
‡ Gas Fuel.
§ Oil Fuel.

TABLE V.

Data for Heat Treating Furnaces.

Parts Treated Name	Purpose of Heating	Temperature		Remarks
		° F.	° C.	
Tool steel	Quench	1425-2350	774-1284	.....
Tool steel	Quench	1425-2350	774-1284	.....
Tool steel	Quench	1425-1550	774- 843	.....
Tool steel	Quench	1425-1550	774- 843	.....
Tinning solder ...	Melt	500	260	.....
Piston pins, cam shafts	Carburize	1700	927	Operates continuously
Cam shafts, gears, etc.	Quench or Draw	1450-1550 or 900-1100	788-843 or 482-593	Operates continuously
Cam shafts, gears, etc.	Anneal	1600	871	Operates continuously
Miscellaneous	Anneal	....	...	Operates continuously
Miscellaneous	Cyanide	1450	788	Operates continuously
Babbitt	Heating	550	288	Operates continuously
Tool steel	Babbitt	1425-1475	774- 802	Cyanide bath
Tool steel	Draw	900-1200	482- 649	Lead bath
Tool steel	Draw	400- 600	204- 316	Oil bath
Valve stems	Quench	1425-1475	774- 802	Cyanide bath
Babbitt	Remelt	800- 900	427- 482	.....

TABLE VI.

Specifications for Heat Treating Furnaces.

Type	Inside Dimensions						Heating Elements Location		Brick or Alloy Hearth
	Length		Width		Height				
	In.	Cm.	In.	Cm.	In.	Cm.	Sides	Bottom	
Car	144	365.8	72	182.9	52	132.1	3 on 1 side	..	Solid Brick
Pot	24	61.0	12	30.5	16	40.6	....	2	....
...	48	121.9	36	91.4	18	45.7	....	2	....
...	30	76.2	15	38.1	18	45.7	....	1	....
...	27	83.8	42	106.7	9	22.9	T & S	2	Brick
...	36	91.4	42	106.7	12	30.5	T & S	2	Brick
...	27	83.8	42	106.7	7	17.8	T & S	2	Brick
...	15	38.1	24	..	15	38.1	T & S	2	Brick
...	15	38.1	24	61.0	15	38.1	T & S	2	Brick
...	26	66.0	60	152.4	6	15.2	T & S	2	Brick
...	24	61.0	60	152.4	8	20.3	T & S	2	Brick
...	44	111.8	60	152.4	36	91.4	T & S	2	Brick
	Diameter								
	In.	Cm.							
Pot	15	38.1			12	30.5	....	1	....
Pot	20	50.8			12	30.5	....	1	....
Pot	20	50.8			12	30.5	....	1	....
...	8	20.3			9	22.9	....	1	....

These furnaces all used oil for fuel.

TABLE VI.

Data for Heat Treating Furnaces.

Parts Treated	Purpose of Heating	Temperature		Remarks
		° F.	° C.	
Con. rods, crankshaft pistons, etc.	Anneal	....	....	Continuous automatic control
Piston pins, tappets, shafts, adj. screws, con. rod bolts, etc..	Quench	1425-1475	774-802	Continuous clean heat used
Piston pins, gears, etc.	Draw	400- 600	204-316	Continuous drawing salt used
Piston pins, gears, etc.	Draw	400- 600	204-316	E. F. Houghton & Co.
Crankshafts, connecting rods	Forge	2000	1093	Continuous drawing salt used
Crankshafts, connecting rods	Forge	2000	1093	E. F. Houghton & Co.
Crankshafts, connecting rods	Forge	2000	1093	.....
Crankshafts, connecting rods	Forge	2000	1093	.....
Crankshafts, camshafts, etc.	Upset	2000	1093	.....
Crankshafts, camshafts, etc.	Upset	2000	1093	.....
Crankshafts, camshafts, etc.	Upset	2000	1093	.....
Crankshafts, camshafts, etc.	Restrike	1600	871	.....
Starting jaws, etc....	Quench	1425-1475	774-802	Continuous cyanide bath used
Starting jaws, etc....	Quench	1425-1475	774-802	Continuous cyanide bath used
Pump shafts, gears, etc.	Draw	900-1100	522-593	Continuous lead bath used
Lead hammers	Melt	1200-1400	649-760	Continuous lead bath used

Table VII.

Specifications for Heat Treating Furnaces.

Inside Dimensions								Heating Elements		Hearth Solid
Length		Width		Height		Diameter		Type	Location	
In.	Cm.	In.	Cm.	In.	Cm.	In.	Cm.			
72	182.9	48	121.9	18	45.7	..	...	Oil	3 on 1 side	No
48	121.9	..	....	..	...	15	38.1	City gas	8 on each side	..
30	76.2	10	25.4	10	25.4	..	...	City gas	5 on each side	Yes
14	35.6	..	...	..	...	10	25.4	City gas	6 all around	..
11	27.9	9	22.9	7½	19.1	..	...	Oil	1 at end	..
90	228.6	60	152.4	18	45.7	..	...	Oil	1 at end	Yes
60	152.4	36	91.4	24	61.0	..	...	Oil	1 front side	Yes
54	132.7	32	81.3	24	61.0	..	...	Oil	1 front side	Yes
15	38.1	..	...	..	...	15	38.1	City gas	3 on 1 side	..
21	53.3	..	...	..	...	33*	83.8	City gas	....	..
24	61.0	18	45.7	12	30.5	..	...	City gas	3 on each side	..
14	35.6	..	...	..	...	10	25.4	Oil	....	..
32	81.3	..	...	..	...	17	43.2	City gas	....	..
15	38.1	..	...	..	...	15	38.1	City gas	3 on each side	..

* Tapering.

TABLE VII.

Data for Heat Treating Furnaces.

Part Treated	Purpose of Heating	Temperature		Remarks
		° F.	° C.	
Steering knuckle*	Carburizing	1700	927	Carburizing tolerance 0.015 lb. (0.007 kg.) Camshafts 0.94 in. (2.38 mm.) 12 hr.; 75 lb. (34.1 kg.) metal; 20 lb. (9.1 kg.) compound per box.
Taper rollers†	Carburizing	1675	913	
Tools	Heating tools	2400	1316	
Tools	Drawing tools	1150	621	
....	Cyaniding	1575	857	2 pots per furnace.
....	Annealing	1550	843	
....	Carburizing	1700	927	2700 lb. (1228 kg.) gross; 1800 lb. (818 kg.) net. 3.5 gal. (13.3 L.) per hr. 6 gal. (22.7 L.) to start. 40-45 gal. (152-171 L.) per heat. 19.2-20.6 per cent gross efficiency. 7.7-10.3 per cent. net efficiency.
....	Carburizing	1700	927	
....	Cyaniding	....	...	
....	Oil temper.	....	...	
Tools	Heating tools	....	...	
....	.....	....	...	
....	Saltpeter pot	1150	621	
....	Cyaniding	....	...	

* Number treated 320. Weight each 1.25 lb. (0.57 kg.).
† Number treated 9,000 to 11,000.

Table VIII.

Specifications for Heat Treating Furnaces.

Inside Dimensions								Heating Elements		Hearth Brick or Alloy
Length		Width		Height		Diameter				
In.	Cm.	In.	Cm.	In.	Cm.	In.	Cm.	Type	Location	
..	...	..	...	12	30.5	12	30.5	Gas	...	....
24	61.0	16	40.6	8	20.3	..	...	Gas	Side under-fired	Brick
18	45.7	12	30.5	4	10.2	..	...	Gas	Side under-fired	Brick
23	58.4	15	38.1	11	27.9	..	...	Oil	...	....
8	20.3	4	10.2	4	10.16	..	...	Gas	...	....
18	45.7	6	15.2	11	27.9	..	...	Gas	...	....
54	137.2	42	106.7	24	61.0	..	...	Oil	Side	Solid br. and lime-stone
*	...	30	76.2	..	...	135	342.9	Ribbon	...	....

* Rotating hearth. Capacity 200 kw.

TABLE VIII.

Data for Heat Treating Furnaces.

Part Treated	Purpose of Heating	Temperature		Remarks
		° F.	° C.	
Tools	Tool oil drawing	450	232	Operated 9 hr./day
Tools	Tool hardening	1450	788	Operated 9 hr./day
Tools	Tool hardening	1450	788	Operated 9 hr./day
Trans. gears	Oil drawing	350	176	Operated 9 hr./day
Tools	High speed tool drawing	2250	1228	Operated 9 hr./day
Tools	High speed tool drawing	2250	1228	Operated 9 hr./day
Parts to be forged	Heat for reforging	1900-2200	1038-1204	Operated 9 hr./day; sometimes 24 hr.
Camshafts, piston pins	Quenching	1450	788	9.68 lb. (4.4 kg.) per kw.-hr. Eff. 71.1 per cent.

TABLE IX.

Specifications for Heat Treating Furnaces.

Type	Inside Dimensions						Fuel	Heating Elements Location
	Length		Width		Height			
	In.	Cm.	In.	Cm.	In.	Cm.		
....	48	121.9	60	152.4	144	365.8	Oil	1 only on side. Some have 2.*
....	48	121.9	60	152.4	144	365.8	Oil	
....	..	....	..	....	...	....	City gas	.....
....	..	....	..	....	...	....	City gas	.....
....	..	....	..	....	...	....	City gas	.....
....	..	....	..	....	...	....	City gas	.....
....	48	121.9	36	91.4	18	45.7	Oil	2 at end bot.
...	30	76.2	15	38.1	18	45.7	Oil	
1st P.	20	50.8	15	38.1	8	20.3	City gas	1 at front.
2nd P.	20	50.8	15	38.1	8	20.3	City gas	1 at front.
H. Temp.	14	35.6	10	25.4	6	15.2	City gas	1 at front.
10 tubes per furnace	144	365.8	18	45.7	15	38.1	Water gas	8 on ea. side†
Incline	108	274.3	16	40.6	12	30.5	Water gas	6 on ea. side†
Incline	72	182.9	15	38.1	6 to 12	15.2 to 30.5	Water gas	5 on ea. side†
....	72	182.9	15	38.1	6 to 12	15.2 to 30.5	Water gas	5 on ea. side†
....	48	121.9	8	20.3	...	....	Water gas	5 burners
....	30	76.2	16	40.6	...	....	Water gas	8-10 burners
....	66	167.6	48	121.9	30	76.2	Water gas	1 burner
....	168	426.8	15	38.1	3	7.6	Elect. ribbon	.....

* Solid hearth. † Hearth not solid.

TABLE IX.

Data for Heat Treating Furnaces.

Purpose of Heating	Temperature ° F.	Temperature ° C.	Physical Properties Obtained	Remarks
Forg.	.....	...	.....	Operates continuously.
Upset.	.....	...	.....	Operates continuously.
Heat. tools	.....	...	.....	
Load pot	.....	...	.....	
Cyanid.	.....	...	.....	
Oil draw.	.....	....	.....	
Draw.	.....	...	.....	
Heat-ing Tools	.....	...	.....	
	.....	...	.....	
	....	...	.....	
Quench. Rollers	1650*†	899	Rollers 430-495 Brinell. Race 70-85 shore.	Capacity 490-525 lb. (223-237 kg.) per hour. Automatic control. 0.56-0.875 in. (14.29-22.23 mm.) stock in furnace 7 min.
Quench. Rollers	1650*	899	Roller 0.45-0.55% C., 0.80-1.05% Cr., 0.15-0.25% Mo.	Capacity 415 lb. (189 kg.) per hour. Automatic control. 0.50-0.56 in. (12.7-14.29 mm.) stock in furnace 9 min.
Quench. Race	1450-1650	788-899	Race straight carbon carbonized.	Capacity 400 lb. (182 kg.) per hour. Automatic control.
Quench. Race	1450-1650	788-899	.....	Capacity 400 lb. (182 kg.) per hour. Automatic control.
Quench. Race	1450-1650	788-899		
Draw.	600-900	316-522		
Carbur.	1700	927	.....	Pot height 22 in. (55.9 cm.) Baffle height 22 in (55.9 cm.) Time in furnace 18-30 hr. Case depth 0.05-0.15 in. (1.27-3.81 mm.)
Quench. or draw.	....	...	.....	575 lb. (261 kg.) per hour. Heating element in each section automatically controlled.

* Temperature of furnace 1,720° F. (938° C.).

† Efficiency 30-31 per cent.

TABLE X.

Specifications for Heat Treating Furnaces.

Inside Dimensions								Cap. KW.	Heating Elements	
Length		Width		Height		Diameter			Type	Location
In.	Cm.	In.	Cm.	In.	Cm.	In.	Cm.			
*	...	24	61.0	..	...	168**	426.7	..	Ribbon	Both sides
*	...	30	76.2	..	...	192**	487.7	..	Ribbon	Both sides
*	...	36	91.4	..	...	216**	548.6	..	Ribbon	Both sides
..	...	..	...	14	35.6	14	35.6	6	Wire	All around
..	...	..	...	16	40.6	24	61.0	7.5	Wire	All around
..	...	..	...	14	35.6	10	25.4	5	Wire	All around
19	48.3	12	30.5	8	20.3	..	...	8	Wire	Sides §
18	45.7	12	30.5	8	20.3	..	...	30	Carbon resister	Sides §
48**	121.9	24**	61.0	30**	76.2	..	...	..	Stock	....
†	...	..	...	24	61.0	16	40.6	10	....	....
†	...	..	...	24	61.0	8	20.3	4.7	....	....
..	...	..	...	18	45.7	15	38.1	12-13 to heat 5 at heat	....	....
179½‡	455.9	40	101.6	10	25.4	..	...	200	Ribbon	Top §
48	121.9	7	17.8	1¼	3.2	..	...	13	Ribbon	Top and bottom
48	121.9	24	61.0	12	30.5	..	...	25	Picture frame construction wire	All around
408**	86.4	60**	152.4	18	45.7	..	...	100	....	....

* Rotating hearth; ribbon extends slightly underneath bottom of hearth.
† Hump type. ‡ Pusher type. § Solid hearth.
** Outside.

TABLE X.

Data for Heat Treating Furnaces.

Part Treated	Purpose of Heating	Temperature		Lb. per kw.-hr.	Eff. Per Cent	Remarks
		° F.	° C.			
Connect. rods	Quench. or draw.	1400	760	11.3 (5.14 kg.)	77	Operates 24 hr./day. 1200 lb. (546 kg.) per hour.
Camshafts, etc.	Quench.	....	...	...	..	Operates 24 hr./day. 1500 lb. (682 kg.) per hour.
Camshafts	Quench.	....	...	...	..	Operates 24 hr./day. 1800 lb. (819 kg.) per hour.
Gear stock	Quench.	....	...	...	..	Operates 24 hr./day.
Gear stock	Draw.	....	...	...	..	Operates 24 hr./day.
Laboratory	.....	....	...	...	..	Operates during day only.
.....	.....	....	...	...	..	Operates during day only.
Tool steel	Heat treat. of tools	2350	1284	...	..	Operates during day only.
Riveter for valve heads	Form. valve heads	....	...	...	..	.....
.....	Quench. and draw.	....	...	...	..	.....
.....	Quench. and draw.	....	...	...	..	.....
.....	Lead pots	....	...	...	..	.....
Connect. rod*	Quench. and draw.	1500 1050-1200	816 567-649	11 (5 kg) on quench	82	.....
Piston pins†	Quench.	1475	802	8.5 (3.86 kg.)	62.3	.....
.....	Draw.	350-700	176-371	...	..	.....
.....	Anneal.	1300	704	...	..	Compensating furnace.

* Weight per part 1.6 to 4.0 lb. (0.73 to 1.82 kg.).

† Number treated per hr. Rollers, 2,000; "Essex," 700; "Super," 475.

Table XI.

Specifications for Heat Treating Furnaces.

Type	Inside Dimensions				Cap. KW.	Heating Elements	
	Length	Width	Height	Diameter		Type	Location
	....	....	14 in. (35.6 cm.)	5½ x 10 or 8½ in. (14.0 x 25.4 or 21.6 cm.)	3.3	....	...
....	....	....	4 in. (10.2 cm.)	4 in. (10.2 cm.)	1.1	....	...
....	....	....	.....	.....	11	....	...
....	....	....	.....	.....	25	....	...
....	....	....	.....	.....	27	....	...
....	....	....	.....	.....	30	....	...
Pusher*	....	....	.....	.....	190	....	...
Pusher*	....	....	.....	.....	160	....	...
....	....	....	.....	168 in.* (426.7 cm.) Outside	190	....	...
....	96 in.† (243.8 cm.)	9 in. (22.9 cm.)	12 in. (30.5 cm.)	.....	..	....	Sides
....	....	....	.....	.....	10	....	...
....	....	....	.....	.....	..	Ribbon	Top
....	....	....	.....	.....	..	Ribbon	Top
....	....	....	.....	.....	150	Ribbon	Top
....	....	....	.....	.....	..	Ribbon	Top
....	....	....	.....	.....	..	Ribbon	Top

* Similar to connecting rod furnace.
† Rotary furnace.

Table XI.

Data for Heat Treating Furnaces.

Part Treated		Purpose of Heating	Temperature		Weight per kw.-hr.	Eff. Per Cent	Physical Properties Obtained
Name	Number		° F.	° C.			
Transm. gears	.....	Quench.	1475	802	8 lb. (3.64 kg.)	58.6	.....
Main drive gear	.....	Quench.	.....		.....	...	.....
.....	.....	Draw.	.....		.....	...	.....
.....	.....	Draw.	.....		.....	...	.....
.....	.....	Draw.	.....		.....	...	.....
.....	.....	Draw.	.....		.....	...	.....
Axles	.....	Anneal. Quench.	.....		.....	...	.....
Axles	.....	Anneal. Quench.	.....		.....	...	.....
Misc.	.....	....	.....		.....	...	.....
Shackle bolts	.....	....	.....		.....	...	.....
.....	.....	....	.....		.....	...	.....
Connecting rod*	32,000/24 hr.	Quench.	1500	816	12 lb. (5.46 kg.)	86	444-512 Brinell
Connecting rod*	32,000/24 hr.	Draw.	800	427	30 lb. (13.64 kg.)	86	277-321 Brinell
Ring gears, brass, etc.	.....	....	.....		.....	150†	.....
Tappets	120,000/ 24 hr.	.....	1500	816	11.92 lb. (5.43 kg.)	85.6	477-555 Brinell
Piston pins	90/hr.	.....	.....		.....	...	.....

* Weight per part 1.125 lb. (0.512 kg.).

† Efficiency supplied by plant using furnace.

Table XII.

Specifications for Heat Treating Furnaces.

Inside Dimensions								Cap. kw.	Heating Elements	
Length		Width		Height		Diameter				
In.	Cm.	In.	Cm.	In.	Cm.	In.	Cm.		Type	Location
..	..	..	..	..	..	..	..	..	Ribbon	.....
..	..	..	..	..	..	..	..	..	Ribbon	.....
..	..	..	..	..	..	..	..	..	Ribbon	.....
..	..	..	..	..	..	..	..	13	.....	.....
..	..	..	..	..	..	..	..	25	.....	.....
..	..	..	..	..	..	..	..	130	.....	.....
..	..	..	..	..	..	..	..	180	.....	.....
..	..	..	..	..	..	..	..	60	.....	.....
..	..	18	45.7	24	61.0	120†	304.8	85	Ribbon	Both sides
..	..	18	45.7	24	61.0	120†	304.8	85	Ribbon	Both sides
16	40.6	12	30.5	6	15.2	..	..	85	Hair pin	Both sides*
..	..	60	152.4	18	45.7	252†	636.1	323	Ribbon	Both sides*
..	..	36	91.4	18	45.7	145†	368.3	150	Ribbon	Both sides
..	..	..	..	24	61.0	30	76.2	12	Wire	All around
..	..	..	..	15	38.1	9	22.9	4.5	Wire	All around
10	Oval 25.4	6	15.2	16	40.6	..	..	4.5	Wire	All around

* Solid hearth.
† Rotary; outside diameter.

TABLE XII.

Data for Heat Treating Furnaces.

Part Treated			Purpose of Heating	Temperature		Weight per K. W. H.	Eff. Per Cent
Name	Number	Weight per Part		° F.	° C.		
Drive shaft, housing, etc.	8000/24 hr.	2.5 lb. (1.14 kg.)	.....	1500	816	12 lb. 5.5 kg.	86
Roller bearings	600 lb./hr. 273 kg./hr.	.....	.....	...	...	...	..
Copper wire	.....	.....	.....	...	...	...	..
Mostly springs	.....	.....	Nitrate pots	...	...	...	..
Rear axles	.....	.....	Draw.	...	...	...	..
Univ. joints,	.....	.....	Quench.	...	...	...	..
.....	.....	.....	Nitrate pots	...	...	...	..
.....	.....	.....	Niag. washer	...	...	...	..
Roller bearing core	210/40 min.	0.5 lb. (0.23 kg.)	Quench.	144	62	7 lb. 3.2 kg.	48.3*
Roller bearing core	420/40 min.	.....	Quench.	144	62	8.5 lb. 3.9 kg.	59.6
Tools	.....	.....	Heat. tools	1550	843	...	..
Front axles	50/hr.	50 lb. (22.7 kg.)	Quench.	...	...	...	..
Camshafts, gears, etc.	80/hr.	10 lb. (4.5 kg.)	Quench.	1575 1425	857 774	...	..
.....	.....	.....	Quench.	...	...	...	..
.....	.....	.....	Quench.	...	...	...	..
.....	.....	.....	Quench.	...	...	...	..

* Power costs $0.011 per kw.-hr.

Table XIII.

Specifications for Heat Treating Furnaces.

Inside Dimensions								Cap. kw.	Heating Elements		Hearth
Length		Width		Height		Diameter					
In.	Cm.	In.	Cm.	In.	Cm.	In.	Cm.		Type	Location	
..	....	..	....	18	45.7	22	55.9	..	Oil	Bottom	..
..	....	..	....	50	127.0	12	30.5	..	Oil	Bottom	..
..	....	..	....	18	45.7	22	55.9	..	Oil	Bottom	..
66*	167.6	24	61.0	24	61.0	..	...	..	Oil	Side‡	§
84*	213.4	24	61.0	30	76.2	..	...	80	Elec. ribbon	Sides	**
†	....	..	....	16	40.6	17	43.2	12	Elec.	All around	..
10†	25.4	6	15.2	11	27.9	..	...	4.4	Elec.	All around	..
†	....	..	....	16	40.6	24	61.0	..	Elec.	All around	..
68*	172.7	38	96.5	23	58.4	..	...	..	Oil	Front sides	††
68*	172.7	38	96.5	23	58.4	..	...	..	Oil	Front sides	††
90*	228.6	38	96.5	23	58.4	..	...	..	Oil	Front sides	††
68*	172.7	52	132.1	23	58.4	..	...	..	Oil	Front sides	††
78*	198.1	48	121.9	23	58.4	..	...	..	Oil	Front sides	††
65*	165.1	36	91.4	13	33.0	..	...	..	Oil	Front‡	§
..	....	..	....	12	30.5	5	12.7	..	Gas	Bottom	..
..	....	..	....	14	35.6	7	17.8	..	Gas	.....	..

* Hearth type.
† Hump type.
‡ Underfired.
§ Brick hearth.
** Solid brick hearth.
†† Semi-heated brick hearth.

TABLE XIII.

Data for Heat Treating Furnaces.

Part Treated	Purpose of Heating	Temperature		Physical Properties Obtained	Remarks
		° F.	° C.		
Misc.	Cyanide	1450	788	.....	9 hr. day, 11 hr. night
Camshaft	Harden.	1400	760	75 Scl. Min.	9 hr. day
Misc.	Lead pot harden.	1380 to 1600	749 to 871	.....	9 hr. day, 11 hr. night
Misc.	Harden.	1380 to 1600	749 to 871	.....	9 hr. day, 11 hr. night
Misc.	Harden.	1380 to 1600	749 to 871	.....	9 hr. day
Trans. gears	Harden.	1380	749	77-83 Scl. Min.	9 hr. day
Trans. gears	Harden.	1380	749	77-83 Scl. Min.	9 hr. day
Misc.	Draw	400 to 1000	204 to 538	.....	.....
Misc.	Carboniz.	1700	927	.....	24 hr.
Trans. gears	Carboniz.	1600	871	.....	24 hr.
Misc.	Carboniz.	1700	927	.....	24 hr.
Misc.	Carboniz.	1700	927	.....	24 hr.
Misc.	Heat treat.	1450 to 1600	788 to 871	.....	24 hr.
Dies	Die harden.	1500	816	.....	9 hr. day
Tools	Cyanide	1450	788	.....	9 hr. day
Tools	Lead pot harden.	1450	788	.....	9 hr. day

Table XIV.

Specifications for Heat Treating Furnaces.

Inside Dimensions								Cap. kw.	Heating Elements		
Length		Width		Height		Diameter			Type	Location	
In.	Cm.	In.	Cm.	In.	Cm.	In.	Cm.			Sides	Bottom
*	...	36	91.4	..	...	14	35.6	200	Ribbon	..	§
*	...	30	76.2	..	...	135	342.9	200	Ribbon	..	§
*	...	30	76.2	..	...	135	342.9	140	Ribbon	..	§
*	...	24	61.0	..	...	94	238.8	140	Ribbon	..	§
..	...	..	...	14	35.6	10	25.4	5	Wire	..	**
..	...	..	...	14	35.6	14	35.6	6	Wire	..	..
..	...	..	...	16	40.6	24	61.0	7.5	Wire	..	Yes
18	45.7	12	30.5	8	20.3	..	...	30	Carbon electrode	..	**
19	48.3	12	30.5	8	20.3	..	...	12.5	Wire‡	..	Yes**
288†	731.5	36	91.4	22	55.9	..	...	...	Oil	5 on each	**
288†	731.5	48	121.9	22	55.9	..	...	...	Oil	5 on each	**
72	182.9	44	111.8	24	61.0	..	...	...	Oil	..	Yes (1) ††
72	182.9	30	76.2	26	66.0	..	...	...	Oil	..	Yes (2) ††
72	182.9	44	111.8	16	40.6	..	...	...	Oil	..	Yes (1) ††
72	182.9	44	111.8	16	40.6	..	...	...	Oil	..	Yes (1) ††

* Rotating hearth type.
† Pusher type.
‡ Heating elements on top.
§ Perforated alloy hearth.
** Solid hearth.
†† Solid brick hearth.

TABLE XIV.

Data for Heat Treating Furnaces.

Part Treated	Purpose of Heating	Temperature		Remarks
		° F.	° C.	
Con. rods, camshafts	Quenching	1450	788	Continuous*
Con. rods, camshafts	Quenching	1450	788	Continuous*
Con. rods, camshafts	Quenching	1450	788	Continuous*
Con. rods, gears	Drawing	950-1100	454- 593	Continuous*
Miscellaneous	Experimental	600-1800	316- 982	.....
Gears, sprockets	Quenching	1420-1470	771- 799	Continuous
Gears, sprockets	Drawing	400- 600	204- 316	Continuous*
Tool steel	Quenching	2100-2350	1149-1288	.....
Miscellaneous	Experimental	600-1700	316- 927	.....
Camshafts, gears	Carburizing	1700	927	Continuous
Camshafts, gears	Carburizing	1700	927	Continuous
Camshafts, etc.	Quenching	1450-1600	788-871	Continuous
Camshafts, etc.	Quenching	1450-1600	788-871	Continuous
Con. rods, crankshafts	Quenching and drawing	900-1550	522-843	Continuous
Con. rods, crankshafts	Annealing and drawing	900-1650	522-899	Continuous

* Automatic control.

BIBLIOGRAPHY.

This bibliography is divided into two sections.

1. Important articles upon the subject from 1910-1924.

2. Articles of secondary importance upon the subject from 1910-1924.

In addition, the following digest is incorporated of the important articles bearing upon the subject of this paper:

Digest of Bibliography.

Attracted by the high quality of work done by the electric furnace in the field of steel melting, metallurgists were led to attempt other operations, such as forging, heat treating, and annealing by electrical means.

Electrically heated heat-treating furnaces may be classified according to the method of heating. A wound furnace is a muffled type, wound with resistance wire or ribbon. In a resistor furnace (of a muffled or semi-muffled type) the heating elements are pressed carbon rings or strips arranged longitudinally. During the war the bare metal resistor type of furnace met with exceptional success. Bare metal resistors, 1 in. x 0.125 in. up to 1 in. x 0.375 in. (25.4 x 3.2 mm. up to 25.4 x 9.5 mm.), were distributed uniformly throughout the furnace, of course in such a manner as not to be touched by the work.

One of the difficulties encountered with the muffled type was the problem of refractories. A temperature of 1,800° F. (982° C.) in the furnace often meant a temperature double that at the bottom of the resistor bed. Silicon carbide is one of the refractories now giving satisfaction for this purpose.

Some of the types of resistors in the bar metal resistor furnaces were given to excessive oxidation. To avoid this a small amount of oil or gas was often admitted, in order to obtain a reducing atmosphere within the furnace. However, in the later types of furnaces, the doors are fitted better, the facilities for loading and discharging have been improved so the door is kept open for a shorter time, and the composition of the resistors is such that in one furnace, for instance, after twenty-five months of

continuous operation no visible signs of deterioration of the resistors were apparent.

In regard to classification, electric furnaces may be grouped according to their design and manner of operation.

The box furnace is shaped as its name indicates. It has one door and is usually loaded and unloaded by hand. For work of dissimilar lengths several box furnaces are placed as units end to end, having dividing doors between them which may be opened. In this manner by opening the doors and heating them all quite long pieces can be accommodated.

The doughnut furnace is round, the bottom of which rotates slowly. Work, small parts such as gears, is piled in one door and after remaining in the furnace the length of time of one revolution of the bed, is taken out through a door adjacent to the first. One man can handle such a furnace without help. The thermal efficiency of this type is quite high.

The car bottom type furnace is one in which the bottom is a snugly fitting platform mounted on wheels. As is apparent, the speed of charging and discharging such a furnace is great. The thermal efficiency is satisfactory if dummy furnaces are used in conjunction, where the heat in a batch of work just pulled preheats a cold charge.

Among the continuous types of furnaces there are various methods of moving the work along, all being dependent upon the size and shape of the work being treated. Some of the devices used are pushers, chain conveyers, gravity roll systems and others. In many cases the heating and quenching are both automatically controlled.

The advantages of the electric furnace are many. The heat is a steady radiant heat, not cyclonic blasts of hot gases. The atmosphere within the furnace is not one of spent products of combustion; hence, the tendency to scale is minimized. The temperature can be automatically controlled to within 4° or 5° C. According to figures from various sources, the deterioration and cost of maintenance is less than for fuel-fired furnaces. The thermal efficiency of the electric furnace is also quite a bit higher than that of other types. However, these last two items may in part at least be due to the fact that an electric furnace is much more carefully constructed than a fuel-fired furnace.

On the other hand, the original cost of the electric furnace is higher. The cost of electrical energy for heating in a properly constructed furnace is slightly greater per pound of steel heated than the cost of oil (most economical of the fuels) after taking into account the different thermal efficiencies of the respective furnaces. It might be advantageous if the work could be so planned as to make the peak demands for power when the central station is not meeting a peak demand from other sources. It would seem, after all, that this disadvantage in price is more than offset by the greater accuracy of control of the furnace, the better quality of the product, and more comfortable conditions for the workmen.

IMPORTANT ABSTRACTS.

Brooke, Frank W. Methods of Handling Materials in the Electric Furnace and the Best Type of Furnace to Use. Trans. Am. Electrochem. Soc., **43**, 149-159 (1923).

General discussion of the various furnaces, that is, plain box type, special box type, the car type, the recuperative and continuous furnaces; their advantages and disadvantages.

The simplest furnace is the box type with one door. For work of varying lengths several box furnaces are built end to end, with dividing doors which are controlled from without.

A car furnace is one in which the bottom is made separately and mounted on wheels. When the charge is heated the car is pulled out and usually placed in a dummy furnace along with a cold charge in order not to waste heat.

In continuous furnaces the simple chain conveyor type has given trouble due to stretching and to the fact that it carries too much heat away. Thermal efficiency 18 per cent. An improvement was to run the chain within the furnace entirely, over cogs which were driven by other chains.

A doughnut furnace has a revolving bottom. Work is loaded in one door and removed from one adjacent after making a complete revolution. Thermal efficiency is high.

The "push" type is quite efficient. It is restricted to work of a uniform shape, which will push in a long column without bridging. The pusher moves longitudinally back and forth in the direction of the slope of the bed of the furnace, the work being pushed down the incline.

The "gravity roll" furnace is used for such pieces as will roll. The work is kept back by a device which allows of a certain predetermined rate of discharge.

Other modifications of these types are discussed.

COLLINS, E. F. Electric Heat, Its Generation, Propagation and Application to Industrial Processes. Trans. Am. Electrochem. Soc., **42**, 113-146 (1922).

Methods for the conversion of electric energy for industrial heating are outlined as follows:

1. Heat may be developed by the passage of current through a solid, laminated or granular conducting medium or "resistor."
   (a) The conducting medium may consist of material that is to be treated.
   (b) The heat developed in the resistor may be transferred to the charge by conduction, convection or radiation, or by all three.
   (c) A readily controllable source of heat may be generated between a fixed and a movable carbon electrode.
2. Heat may be developed by a flow of current through gas or air.
   (a) Arc furnaces in which arcs play between two or more electrodes near the material to be treated or between one or more electrodes and the work to be treated.

Various conceptions of heat and energy are given along with a detailed discussion of the fundamental ideas on heat transmission and heat emissivity.

Various advantages of the bare metal resistor as over the muffled resistor are mentioned.

Entire cost of heat treating electrically was cheaper than oil heating by 6/1000 of the cost of production. Electric power 1 cent per kw.-hr. and oil 5 cents per gallon.

COLLINS, E. F. Electrical Energy Economical for Heat Treating. Trans. Am. Soc. for Steel Treating, **5**, 67 (1924).

Relative costs of electric and fuel fired furnaces must not be based entirely on a B.t.u. basis. Other factors must be considered, such as depreciation, efficiency, overhead, etc. Gives figures on a B.t.u. basis: *oil fired furnace*—oil 7c/gal. 20,000 B.t.u. supplied to furnace, thermal efficiency 16 per cent, heat utilized 3400 B.t.u., cost $0.01; *electric furnace*—coal at $5/ton. Generating efficiency 1.5 lb. coal = 1 kw.-hr. 3840 B.t.u. delivered as current from 20,000 B.t.u. heat at central station. Thermal efficiency of furnace 80 per cent, heat utilized 3400 B.t.u., cost $0.01.

Gives another illustration arriving at same conclusion for indirect oil burner (eff. 12 per cent) *vs.* an electric box oven for enameling (eff. 28 per cent).

General discussion of advantages of electric furnace, especially of the bare metal resistor type, in such respects as temperature control and atmospheric conditions, no overheating, etc. Actual operation for a month, (furnaces hot when charged) heating work to 1450° F. (788° C.) Furnace 6 ft. diameter, 24 ft. high, using a voltage of 440, 60 cycles and a capacity of 400 kw. Energy cost per ton of steel $1.52 at $0.0085 per kw.-hr.

COLLINS, E. F. Metallic Resistor Electric Furnaces for Heat Treating Operations. General Electric Review, **23**, 433-41 (1920).

Type of furnace developed during the war is a bare metal resistor in shape of a ribbon 1 x 0.125 in. (25 x 3.18 mm.), uniformly distributed throughout the furnace. There is no appreciable deterioration of these heating coils. Being bare, the temperature of the furnace is controlled more quickly and accurately, the desired temperature is more quickly reached.

A description of various types of furnace is given, showing how resistors should be placed in order to obtain a uniform distribution of heat.

The cost of hardening by heating to 1450° F. (788° C.) and drawing to 1100° F. (593° C.) at $0.0085 per kw.-hr. amounted to $2.76 per ton in October, 1918.

Tests on a vertical furnace, heating to 1450° F. (788° C.) Furnaces 6 ft. (1.83 m.) diameter x 24 ft. (7.3 m.) high, 440 volts, 60 cycles, capacity 400 kw. Average pounds per kw.-hr., 11.25; kw.-hr. per ton, 173. Energy cost per ton at $0.0085/kw.-hr. = $1.52.

COLLINS, E. F. Some Observations on Furnaces and Fuels, Including the Electric Furnace for Heat Treating. Trans. Am. Soc. for Steel Treating, **4**, 709-726 (1923).

Furnaces should be fitted to the process rather than the process to the furnace. Discussion of adaptability of electric furnace of the resistor type for carbon steel treatment. Advantages of electric furnace: (1) High temperature quickly obtained. (2) Accurate automatic temperature control. (3) Uniformity of product. (4) Furnace free from gases. (5) Heating by uniform radiation rather than cyclonic blasts of gases. (6) Greater ease in handling work.

Figures are quoted for large dies heated to 1800° F. (993° C.) with automatic temperature control. Cost $0.199 per pound steel heated *vs.* oil fired furnace $0.317 per pound steel heated. Upkeep of electric furnace is low.

DUFRESNE, A. O. Electric Furnaces for Heat Treatment of Steel. Electrician, **83**, 375-377 (1919).

The inception of electric furnaces for heat treating arose, without doubt, from the excellent results obtained by electric melting.

Historical methods of hardening points of tools:

1. Connect one pole of dynamo to tool and other to cast iron pot containing K_2CO_3 solution. Tool then partially immersed. When tool was heated, current was broken and solution did the chilling.
2. Tool placed on refractory bed and an arc was started at point.
3. Tool mounted on a mandrel which formed part of the circuit of a single turn low voltage transformer. Current maintained until the color of the tool was the desired shade. This was used for tempering milling cutters, etc.

Present methods:

1. Electric furnaces. The arc is used differently than in melting furnaces.
2. Resistance furnaces:
   (a) Dry furnaces.
   (b) Salt bath furnaces.

Wound furnaces (dry or wet) wire.

Resistor furnaces (pressed C rings or carbons arranged longitudinally).

Description of Wild-Barfield patent salt bath furnace. Instead of determining temperature by means of a pyrometer, an automatic device determines the point of decalescence—a point at which steel loses its magnetism. Another device automatically removes and quenches the piece.

HESS, H. L. The Electric Arc Melting Furnace and the Central Station Electric Company. Trans. Am. Electrochem Soc., **37**, 413-430 (1920).

Semi-popular treatise on amounts of current used in various types of electric furnaces, especially those for melting iron and steel. Suggestions as to safeguarding the consumer against using more power than his "peak load" allows him, thus avoiding trouble with the central station.

A desirable load from the power producers' standpoint is one that fully pays its proportion of fixed charges (interest, amortization, taxes, etc.), or one that permits of lower operating cost during a 24-hour period, because of absorption of overhead charges during off-peak periods.

Suggestion as to prevention of allowing power demand to exceed peak demand allowed—to have some type of signal device that will flash a series of colored lights or sound a gong when 10 per cent below established demand, and again when the demand is reached.

IPSEN, C. L. Selection of Electric Furnace for Steel Treating. Trans. Am. Soc. for Steel Treating, **3**, 720-728 (1923).

Improved design, automatic control and favorable atmospheric conditions make the electric furnace more economical than furnaces fired with gaseous, liquid or solid fuels, when a high-grade material is desired.

The design of electric furnaces is so improved that they may be had for all purposes.

An electric furnace may be so situated as to fulfil best its mission as a link in the manufacturing chain. It does not have to be set apart because of noise, obnoxious fumes and intense waste heat.

The atmosphere in the furnace room is better in the case of an electric furnace. Tests were made near each of two similar furnaces, one electric and one fuel fired.

	Electric Furnace	Fuel Furnace
Temperature, °F	79	121
Temperature, °C	26	49
CO_2, per cent	4	7
Humidity, per cent	60	23

Various types of furnaces are discussed, such as the box type, the car type, revolving hearth and the pusher type. All have bare metal resistors.

The furnace described for annealing was operated at night in order to profit by lower power cost.

In a rotary furnace one man can load and unload the work without aid. One user of this type of furnace saved 2.5 cents per part on heat treating labor alone, and the electricity for heating cost less than 2 cents per part.

IPSEN, C. L. Cost of Heat-Treated Parts Reduced to a Minimum by Electric Furnace. Elec. World, **79**, 1125-1126 (1922).

Detailed cost figures and comparative figures for oil furnace and electric furnace are given. In the electric furnace in 25 months the cost due to deterioration of resistors was nil. The only attention necessary was the occasional oiling of the automatic control apparatus. In some parts of the country electric power is cheaper than oil to run equivalent furnaces.

Total cost of electricity in heat treating dies equalled 0.0033 per cent of ultimate cost of dies. When figuring on cost of power, other factors must be considered, such as reduction of rejected parts, etc.

In the case of this die-heating furnace the cost of the electricity is virtually the same as the cost of oil. Tests were run for General Electric Company on oil furnaces and electric furnaces, similarly constructed. Oil furnaces cost 23 cents/hr. with oil at 13 cents. Electric furnaces cost 1 cent/hr.; power rate 1.5 cents per kw.-hr.

At Standard Equipment Company, Cleveland, a rotating annular ring hearth was used for heating gears (the last item in table below). 3-phase, 220-volt furnace used. Cost on 30 days operation: No. gears, 9,510; wt., 39,107 lb.; cost, 3 cents per gear. "The cost of oil used in heating these same gears is 0.5 cent, or approximately one-fifth the cost for electricity. Here, again, the increased cost is offset by the reduction of rejections and the lower cost of subsequent operations."

Advantages of metallic resistor type of furnace are: (1) Low temperature of heat source, (2) accurate and reliable automatic temperature control, (3) uniform and unvarying temperature, (4) absence of severe oxidizing and corroding, common to some fuel fired furnaces. No overheating.

Cost figures for hardening and drawing steel show that subsequent operations must be considered.

Cost of Heat Treating Various Articles.

Part	Factory cost of parts	Cost of heat treating	Cost of electricity for heat treating	Electricity in per cent of total cost
1. Segment combination die..	$1,380	$13.50	$4.16	0.3
2. Segment combination die..	1,138	12.00	3.70	0.32
3. Round blanking die.....	638	5.03	1.50	0.23
4. Segment blanking die.....	782	9.45	2.92	0.37
5. Die	795	10.53	3.43	0.43
6. Die	875	8.66	2.67	0.3
7. Gear	234	13.00	3.70	1.5
8. Gear	268	15.00	4.44	1.7
9. Gear	338	21.00	6.25	1.8
10. Gear	391	26.00	7.60	1.9
11. Gear	455	30.00	9.06	2.0
12. Die block	110	1.75	0.65	0.6
13. Gear*	5†	....	0.03	0.6

* Hardening only, no draw. † Estimated.

LITTLE, G. M. Builds Electric Forging Furnace. Iron Trade Review, **69**, 1689-1692 (1921).

Discusses difficulties encountered in construction of C resistor-type furnace for heat treating and forging work. Gas or oil used to prevent resistor oxidation. Insulation problem solved. Need for electric furnace due to lack of natural gas and need for close control. Advantages of electric furnace: Does not radiate much heat, higher temperature can be obtained. Capable of large outputs. Descriptions of furnaces and component parts.

SCOTT, W. S. Electric Furnace for Forging Steel. Iron Age, **101**, 1676-1677 (1918).

Description and data concerning furnace. For various purposes, including forgings, the temperature was 1800° F. (982° C.) This temperature in the furnace corresponded to a temperature of 3600° F (1982° C.) at the bottom of the resistor bed. Experiments were conducted at Westinghouse Electric Company that led to the adoption of silicon carbide as a resistor. SiC has a decomposition temperature of 4000° F. (2204° C.) and has a high tensile strength, so that the roof of the heating chamber as well as the hearth can be constructed of it.

WEST, CLARENCE JAY. The Electric Furnace as Applied to Metallurgy. Trans. Am. Electrochem Soc., **38**, 365-456 (1920).

A complete bibliography from 1900 to 1919 on the construction and operation of electric furnaces, as applied to the metallurgy of iron and steel and the non-ferrous metals.

WOOD, HAROLD F. Determination of Heat Treating Costs. Am. Soc. for Steel Treating, **2**, 710-717 (1922).

In most plants the cost of the heat treating department is the least known. One of the important items in cost determination in the heat treating department is the proper distribution of the departmental burden on the various units of the department, so that each one will bear its proper share. He describes a method of dividing the department into "burden centers," each one of which is charged up with items such as the following: Interest, taxes, depreciation and repairs, land and building factor, fixed charge on equipment, indirect labor such as janitor service, supplies such as small tools, paint and oils, etc., power and fuel, general factory burden, overhead such as clerks and stenographers, and various miscellaneous charges.

Each operation, whether productive or non-productive (such as trucking and handling), is charged to its burden center.

From such data Mr. Wood determines the cost of each operation in the heat treating department.

ARTICLES OF SECONDARY IMPORTANCE.

BAILY, T. F. Electric Furnaces of the Resistance Type Used in the Production of Essential War Materials. Trans. Am. Electrochem. Soc., **35**, 411 (1919).

BAILY, T. F. Data on the Operation of Electric Furnaces. Elec. World, **71**, 780-781 (1918).

Ratings and uses of resistance-type furnaces are given.

BAILY, T. F. Electric Furnaces for Reheating, Heat Treatment and Annealing. Met. Chem. Eng., **13**, 558-564 (1915).

A general discussion.

BAILY, T. F. Electricity for Heat Treatment in the Steel Industry. Elec. Rev. (Chicago), **75**, 149-154 (1919).

Descriptions and comparisons.

BAILY, T. F. Electrically Heated Soaking Pits. Iron and Steel of Canada, **2**, 180-186 (August, 1919).

Applications of Baily furnace.

BAILY, T. F. Electric Furnaces of the Resistance Type for Heat Treating. Elec. Furnace, **45**, 3-5 and 18-19 (1920).

Survey of types of heat treating (electric) furnaces.

BAILY, T. F. Annealing and Heat Treating of Steel and Melting of Non-ferrous Metals in the Electric Furnace. J. Cleveland Eng. Soc., **10**, 81-92 (1917).

Resistance furnace.

BERRY, E. R. Clear Fused Quartz Made in the Electric Furnace. Trans. Am. Electrochem. Soc., **45**, 511 (1924).

BIDWELL, CHAS. C. Wire and Ribbon Wound Resistance Furnaces. Sibley Journal of Engineering, **36**, 119-121 and 129 (June, 1922).

Temperature range determined choice of resistor refractory and insulation. Temperature distribution determines shape of furnace, manner of winding, heating elements and placing thermal insulation.

CHANEY, C. E. Design of Electric Annealing Furnaces. Foundry, **49**, 720-723 (1921).

Theory of malleable iron annealing described on basis of Fe-C equilibrium diagram. Data are given on physical properties of castings annealed 42 to 50 hours, completely annealed without scale.

CLARK, A. M. Vertical Cylindrical Electrical Furnaces for Heat Treating and Shrinking. Chem. Met. Eng., **21**, 205-207 (1919).

During the war two types of furnace were developed: A high temperature resistance furnace, 1800° F. (982° C.) for tempering, hardening and for gun forgings, and a low temperature furnace, 950° F. (510° C.) for shrinking jackets over gun barrels, etc. The latter furnaces were often built in sections.

Heating unit, calorite ribbon.

Detailed description of construction and control are given.

CLARK, A. M. New Type Electric Furnace. Iron Age, **103**, 1502 (1919).

Description of furnace for heat treatment and shrinking.

COLLINS, E. F. Electric Heat for Thermal Processes. Jour. Ind. and Eng. Chem., **14**, 1014 (1922).

The uses described are for baking auto engine cores; japanning ovens; glass annealing ovens; muffled arc for melting brass and copper, in all of which uses electric heat has proved efficient. Also for baking vitreous enamels; cartridge unit heaters and glue melting pots.

CONE, E. F. Electric Furnace and Heat Treatment. Iron Age, **108**, 643-648 (1921).

Lists of the number of electric furnaces in use.

CUTTS, V. O. Baily Electric Furnaces. Electrician, **83**, 405 (1919).

Brief description of the tilting, annealing and the heat treating furnaces.

DAUCH, ALAN D. Rotary Electric Furnace Shows Marked Advantages. Elec. World, **78**, 565-566 (1921).

Description of furnace to be used for annealing, heat treating and carburizing.

DAUCH, ALAN D. 17.4 lb. Steel Annealed per kw.-hr. Elec. World, **79**, 579-580 (1922).

Several thousand tons turned out without a single rejection. Inherent troubles with fuel fired ovens have been overcome at plant of Fowler and Union Horse Nail Company, Buffalo, New York.

DAUCH, ALAN D. Regenerative Car Furnaces. Iron Age, **109**, 1717-1718 (1922).

Description and operation of car-type electric furnace for annealing wire. Cold wire is placed in pre-heating chamber, where it absorbs heat from a charge that is cooling. Then it is placed in the heating chamber. After this it is moved into the cooling chamber. All conveying is automatically done by controls at end of room, from which point the various doors are also controlled. Thermal efficiency is high.

FERGUSON, J. B. Temperature Uniformity in a Laboratory Electric Furnace. Phys. Rev., **12**, 81-94 (1918).

Long discussion.

GATEWARD, W. A. Nichrome and the Electric Furnace. Proc. Steel Treating Research Soc. and J. Am. Steel Treaters Soc., **2**, 16-17 and 37.

Electric heat treating furnaces made by Hoskins Mfg. Co.

HANSEN, F. A. Electric Heating Applied to the Steel Industry. Assoc. Iron and Steel Elec. Eng., **4**, 765-776 (1922).

A description of various types of electric heating furnaces adaptable to steel plants. Core ovens will produce 12 lb./kw.-hr. with electric furnaces at 87 per cent efficiency. Fuel furnaces operate at 15 per cent efficiency. $1 worth of electricity equals $3.23 worth of gas or $1.08 worth of oil. The use of electricity at 1 cent per kw.-hr. is economical and produces a better product.

HENDRICKSON, B. Tempering Tool Steel in an Electric Furnace. Chem. Eng., **16**, 149 (1913).

Advocates electric furnace equipped with a pyrometer to remove guessing as to temperature.

HILSE, K. Electrical Heat Treating Furnaces (fused $BaCl_2KCl$ bath). Elektrochem. Z., **26**, 143 (1920).

Description and 3 illustrations of furnace.

HIRSCH, A. Electric Furnaces for Heating Steel. Iron and Steel Institute, Carnegie School. Mem., **6**, 68-93 (1914).

Useful data.

HOLDEN, GEORGE H. High Temperature Electric Heat Treating Furnaces. Sci. Am. Monthly, 440-444 (May, 1920).

Popular.

LITTLE, G. M. An Electrically Heated Forging and Heat Treating Furnace. Trans. Am. Soc. for Steel Treating, **2**, 228-236 (1921).

An account of the development of a resistance type electric furnace for high temperature work.

MILLER, D. D. Electric Treatment of Airplane Forgings. Iron Age, **102**, 381-385 (1918).

Detailed description of installation of Baily furnace for heat treating axle forgings, at Ingalls Shepard Forging Co.

MILLS, GEORGE P. Electricity Applied to Annealing. Foundry, **49**, 366-368 (May, 1921).

Pit furnaces heated electrically by resistance ribbon are described. Pyrometer control.

MILLS, GEORGE P. Electric Annealing and Heat Treating Furnace. J. Engineers' Club of Philadelphia, **38**, 25-31 (1921).

Nichrome resistor type of electric furnace.

PETTY, D. M., and STANDING, A. J. Electrical Applications in a Bethlehem Steel Plant. Blast Furnace and Steel Plant, **11**, 304-310, 368-377 (1923).

PRENTISS, F. L. Uses Electric Furnace in Malleable Foundry. Iron Age, **103**, 537-543 (1919).

Heat treatment done in a Baily electric furnace.

SABERSKY, E., and ADLER, E. New Electrical Hardening Furnace. Trans. Faraday Soc., **5**, 15-36 (1910).

Description and operation of a fused metallic salt furnace. Historically interesting. The work, temperatures and salts used were as follows:

Tempering steel	200- 580° C.	$NaNO_3$ and KNO_3
Annealing copper alloy, etc....	650- 900° C.	NaCl or NaCl and KCl
Hardening C steels.....	750-1100° C.	KCl and $BaCl_2$
Hardening alloy steels.....	1050-1350° C.	$BaCl_2$
Hardening alloy steels.....	1500-1600° C.	CaF_2 or MgF_2

Discussion of operation of this furnace and of advantage of electric furnaces in general.

Scott, W. S. Development of the Electric Furnace for Annealing, Treatment and Forging of Steel. Chem. Met. Eng., **19**, 86-89 (1918).

Scott, W. S. Industrial Electric Heating. Elec. J., **19**, 203-208 (1922).

Furnaces for various purposes are considered.

Scott, W. S. Operating Costs and Industrial Heating. Elec. J., **21**, 283-284 (1924).

General discussion of applicability of electric heat to railway traction companies.

Swoboda, H. O. Electric Heaters for Heat Treating Furnaces. Am. Drop. Forger, **6**, 540-543 (1920).

Carbon and graphite resistors used with success.

Swoboda, H. O. Recent Developments in Electric Heat Treating Furnaces. Forging and Heat Treating, **7**, 83-85 (1921).

Applications and data. Classification of electric heat treating furnaces as to resistor construction, resistor material, charging and operating control.

Unger, M. Electric Hardening Furnaces. Gen. Elec. Rev., **16**, 158-163 (1913).

Review of types of furnaces for this purpose; gives description of fused salt furnace 8 x 8 x 8 in. (20 x 20 x 20 cm.) for hardening tools. Advantages over lead bath furnace: Slower, more uniform heating; steel does not float; due to salt solidfying, cracks in crucible are self-healing. Heat is produced by resistance of fused salt—electrodes are inside of crucible. This is claimed to be much superior to external heating.

Wright, C. E. Electric Heat Treatment of Gun Forgings. Iron Age, **103**, 673-678 (1919).

Description of installation at Tioga Steel and Iron Co., Philadelphia.

ANONYMOUS.

A Modern Tool Room Heat Treating Plant. Ry. Mech. Engineer, **94**, 289-291 (1920).

Electric furnaces and pyrometers at Ft. Wayne shops of Penna. Railroad.

New Electric Spring-Treating Furnaces Increase Production. Automatic Manufacturer, **42**, 22-23 (1920).

Details of ovens, heated and controlled electrically at Bridgeport Spring Company.

Plant of the Electric Furnace Company. Brass World, **15**, 61-63 (1919).

Manufacture of Baily furnaces for electric heat treating and annealing.

Wild-Barfield Electric Furnaces ("Stannas" Resistance Wire Furnaces). Electrician, **85**, 212-213 (1920).

Description and illustrations of "Stannas" furnaces for annealing and heat treating.

Portable Electric (Baily) Furnace Used to Heat Sheet Metal. Elec. Rev. (Chicago), **79**, 213 (1921).

A Baily furnace specially constructed so that it could be transported by crane to various parts of the plant. It is used for auto body and fender stampings. Rating 100 kw.; hearth 40 x 79 in. (102 x 200 cm.); door opening 40 x 26 in. (102 x 66 cm.); capacity 750 lb. (340 kg.) per hr. to 1800° F. (983° C.) Uniform temperature obtained; scaling reduced.

Small Semi-Cylindrical Heat Treating Furnace. Elec. Rev. (Chicago), **79**, 602 (1921).

Gives a design of a small furnace free from objections usually raised against furnaces of this size.

Resistor Furnace Operates at 1,290°. Elec. World, **82**, 1278 (1923).

Tools are automatically conveyed through the furnace and extruded into quench. Furnace consists of two chambers; main heating chamber and final heating chamber.

Electric Treatment of Forgings. Elec. World, **75**, 67-68 (1920).

Description of operation of Baily furnace designed by Electric Furnace Co., of Alliance, Ohio. There were few "rejects," and these were due to variation in the metal. The set-up included a pre-heater, a heating furnace and a quench. The original feeding is done by hand, the remaining operations and the temperature control are automatic.

Electric Forging Furnaces. Elektrochem. Anzeiger, **38**, 361 (1921).

The Wild-Barfield Electric Muffle. Engineering, **106**, 143 (1918).

Description of muffle hardening furnace.

Electric Hardening Furnace. Iron Age, **92**, 174 (1913).

A large furnace; uses a pre-heater. A "wet" type—KCl and $BaCl_2$ are used in varying proportions to give correct temperature. Illustrations.

New Heat Treating Furnace. Iron Age, **108**, 665 (1921).

Description and illustrations of a revolving hearth furnace for automobile parts.

Nouveaux fours Electriques a Resistance pour le Traitement Thermique de l'acier. L'Industrie Électrique, **30**, 405-407 (1921).

Description of vertical and horizontal continuous furnace developed during the war.

New Electric Annealing Furnace (Niagara Falls). Metal Industry, **12**, 279-280.

Description. An automatic furnace in which material is automatically fed and quenched. (Baily furnace.)

Baily Electric Furnace for Heat Treating Shells. Met. Chem. Eng., **18**, 156 (1918).

Detailed description. Two furnaces with a quench between them. Timing apparatus blasts as soon as metal strikes quench. Water flows for predetermined time, then pusher moves work into second furnace.

DISCUSSION.

F. S. Weiser[5]: Dr. White says that it is very difficult to get costs where oil heat is in use. I realize that that is true. There are a great many difficulties in regard to getting costs, especially when you have a large plant, in which your oil is handled from a central pumping system and pumped all over the plant, and at various points has different temperatures and different specific gravities. We have found no satisfactory way of measuring the oil consumption. The only good method, we have found, is to put in a weighing tank and actually weigh the oil. I would like to know if there is any good, cheap, convenient way of measuring oil under conditions such as I have outlined.

Prof. White mentions 1800° F. (982° C.). I have heard of a new heating unit that has come on the market in the last year or two which, I believe, is a molded carborundum unit, which is said to be good for much higher temperatures than 1800° F. (982° C.) I wonder if anybody here who has had any experience with that new unit could tell us anything about it.

C. A. Hill[6]: We have found that oil meters give us close records of oil consumption. Each department, and in some cases,

[5] Research Engr., Scoville Mfg. Co., Waterbury, Conn.
[6] Mueller Co., Port Huron, Mich.

each large furnace, is metered. We always use the smallest size meter which will do the work, and always connect two of them tandem on each line. Differences between the two should not be over 5 to 8 per cent. The sum of all these line readings will check with two meters connected in a similar manner on the main supply.

E. F. COLLINS[7]: In connection with Prof. White's paper, in general I would say, first, that I am heartily in favor of educational work in the application of the electric furnace, as has been suggested. Such educational work should teach some of the following general principles:

The electric furnace should be used only when a complete analysis of the local conditions surrounding its use show it to be a superior economic tool over the fuel-fired furnace. In other words, when the electric furnace shows the highest over-all economy in industrial processes, then electric heat with its intrinsic characteristics such as "form value," heat control, etc., rather than fuel heat with its low B. t. u. costs should be used.

As regards the proper selection of a furnace for a given process, the furnace should be fitted to the process rather than to attempt to fit the manufacturing process to the furnace.

We are just beginning to appreciate that heat application in this country has been too long, for the greater part, in the hand of the promoter rather than of the competent engineer, who is familiar with the possibilities of all forms of fuel as well as electricity.

The furnace engineer of today recognizes and distinguishes between heat quantity and heat intensity, and visualizes the B. t. u. values separate and apart from heat control, heat potential, or thermometer readings. While heat phenomenon was one of the earliest recognized by man, yet his thoughts ran along the line of heat intensity, as indicated by the thermometer, until recently.

Our thermal engineer now knows that the B. t. u. has a floating value, and in consequence knows that no one heat energy source is superior for economical heat results at all times and in all places.

The principal conditions under which heat energy assumes

[7] Consulting Engr., Industrial Heating Dept., General Electric Co., Schenectady, N. Y.

various values or has a fluctuating intrinsic value may be given as follows:

1. Energy value stored in fuel yet in the earth.

2. Commercial value at burner.

   a. Based on B.t.u. content.
   b. Based on B.t.u. heat units generated.
   c. Based on B.t.u. heat units available for work.
   d. Based on B.t.u. heat units utilized by work.

3. Engineering value.

   a. Utilization of heat values.
   b. Heat generated value.
   c. Heat application and control value.
   d. Heat conservation value.
   e. Heat temperature control value.
   f. Miscellaneous values.

4. Form value.

   a. Saving of labor.
   b. Saving in storage, floor space.
   c. Miscellaneous savings.

   "Form value" may be defined as an advantage resulting from physical condition or chemical combinations in a heat energy source, entirely separate and apart from B.t.u. content, such that an advantage comes about in the application of this heat to useful service. The price of fuel or electricity type furnace, and the heat balance for the process, are excluded from this conception of "form value."

5. Specific intrinsic value for the process.

   This comes from unusual or local conditions or exacting requirements, advantages in operation involving the personal element of operators, labor of handling product for heat treating, designs giving unusual quality, production, efficiency, costs, etc.

6. "Over-all" costs.

   This final value is a composite made up of the foregoing and is the true economic value of the heat energy source corresponding for a given heat energy application. *This is the floating value of the B.t.u. for this specific process.*

There is no direct constant relation between the calorific value of heat source and the "over-all" cost in industrial heating. The "over-all" cost is a function of (1) the character of the "heating cycle" required by the product under manufacture; (2) the equipment provided for the application of heat; (3) the conditions

under which the equipment is operated; (4) the efficiency of operators; and (5) the cost of the heating medium, be it electricity or fuel. All these factors combined determine the factory costs, whether fuel or electricity is used. The quantity consumed affects the cost of production, usually, to a lesser degree than any other single factor listed above. Fuel consumption, for a given process, may easily be twice as great in one furnace as in another doing the same work but having a more efficient design. Again, it is true that a well-designed equipment may be so inefficiently operated (especially in fuel furnaces) that it consumes double or treble the quantity of heating fuels or electricity that a watchful and highly efficient operator would use for the same production with correct methods of operation.

And since, when all has been said and done, the human element may materially modify results, attempts should, therefore, be made to take, as far as practical, every opportunity offered to minimize the effect of human manipulation. I refer to such things as perfect conversion of heat, met with in the electric furnace, and the automatic control of power or temperature, which is almost perfectly accomplished in the present-day electric furnace.

WRONG DEDUCTIONS IN COMPARING HEAT SOURCE EFFICIENCIES.

Many wrong deductions regarding the efficiency of electric heating come from comparing an inefficient electric furnace, perhaps improperly operated, and in design not suited to the specific process and manufacturing conditions with a fuel-fired furnace which is suited to the fuel, and the process, and which is more efficiently operated. The difference in economy resulting is too often charged to the difference between electric heating and fuel heating.

In order to forestall charges of misapplication of a "fuel," designs must take advantage of the *"inherent characteristics"* of electricity or a fuel, as the case may be. Again, furnaces of the box type, used by intermittent charging, should not be compared to "tunnel" type continuous conveyor type, neither should "non-compensated" or "non-regenerative" furnaces be compared to compensated or regenerative or reflexed heat types and equal performance expected. In such cases we should look for a more or less wide variation in performance between the different types

when used under the same conditions. The lowest "over-all" cost of production will usually demand one particular type, depending upon requirements of the product.

ELECTRIC FURNACE AND CONSERVATION OF ENERGY.

Fuel is used with an average efficiency the country over of about 10 per cent in metallurgical furnaces. An average of 250 miscellaneous oil-burning furnaces gave a thermal efficiency of 9.2 per cent.

Compare the above 9.2 per cent to 10 per cent, and that of the electric furnace fed from a good steam-electric plant which delivers 12 per cent of the fuel at the bus, or of a super-steam turbine electric plant, which delivers 19 per cent of the fuel B. t. u. at the bus, or the mercury boiler plant which promises 30 per cent at the bus. The heat-treating furnace with a thermal efficiency of 80 per cent will in the first case utilize 9.6 per cent of the fuel in useful work, while in the second case it will deliver 15.2 per cent and in the third and last case, at the same efficiency, it will deliver to the charge to be heated 24 per cent of the energy of the coal burned under the boiler, and it becomes evident that electric heat stands ready to conserve coal and oil supply.

In conclusion, I would like to impress upon all two general observations, and if this discussion has clearly and permanently established the importance of these observations, its main object will have been achieved. These observations are:

First: The B. t. u. has a fluctuating value, and its value becomes fixed only for fixed conditions surrounding its utilization for each heat source.

Second: The highest "over-all" economy in heat treating processes frequently demands electric heat with its intrinsic characteristics, such as "form value," heat and temperature control, etc., rather than fuel heat with its low B. t. u. cost.

G. M. Berry[8]: I agree heartily, and I want to endorse what Mr. Collins just said about it being impossible to decide, without considering all the elements that enter into any problem, what type of furnace should be used. I want, primarily, though, to ask a

[8] Chief Chemist, Halcomb Steel Co., Syracuse, N. Y.

question concerning Prof. White's paper; that is, has he any data with reference to the flexibility of electric furnaces as compared with oil furnaces or coal-fired furnaces or coke-fired annealing furnaces? That is to say, how do the operating costs of the two types compare when we take into account week-end shutdowns?

In the annealing of alloy steels the heat treating temperatures change by a considerable number of degrees from one lot to another, necessitating in some cases raising the temperature of the furnace for a succeeding lot, and in other cases lowering the temperature. What is the flexibility of the electric furnaces as compared with the fuel-fired furnaces?

A. E. WHITE: I have found no data which set forth increased flexibility due to the use of electric furnaces. Up to 1700° F. (927° C.), the practicable limit of metallic resistors, one can get the same if not a greater flexibility with electric furnaces than one can get with oil or gas-fired furnaces.

With properly built electric furnaces of the non-compensating types, efficiencies of 40 per cent and 85 per cent are obtained. The former is the value secured when starting with a cold furnace, and the latter the value when starting with a hot furnace. Doubtless the same relative difference, though not the same percentage difference, holds true for the gas and oil-fired furnaces. It is true that electric furnaces of the resistor type will not heat metal quite as rapidly as it is possible to heat it in oil or gas-fired furnaces. It is questionable if the more rapid rate of heating in the gas and oil-fired furnaces is not more detrimental than beneficial. As a general principle, the slower the metal can be brought up to heat, the better it is for the metal. Likewise, the more closely metal can be held at the desired temperature, the better it is for the metal. Both of these conditions are within the scope of the electric furnace. Gas and oil-fired furnaces can not be operated within such close limits as are possible in the case of the electric furnaces, and for that reason metal heated in such furnaces is not as satisfactorily treated as metal heated in electric furnaces.

One or two resistor elements are now on the market which claim to make it possible to maintain satisfactorily temperatures above 1800° F. (982° C.) The elements themselves appear to be satisfactory. The difficulty experienced today through the use

of these elements is said to be due to overheating at the zone of contact between the conductor and the element. We have been advised that this difficulty has been satisfactorily overcome. It is a matter which with proper concentration of effort should offer no undue difficulties to its solution.

COLIN G. FINK[9]: May I ask Prof. White whether he knows of commercial installations in which furnaces are heated by both electricity and by fuel. In order to bring the heat of a muffle furnace up faster, we have used a gas flame or an oil flame to heat the cold muffle. You can not use both electricity and fuel at the same time; it is not good for the resistor. You must allow a little time to elapse after you are through pre-heating with the oil burners to permit the residual gas to escape before closing the electric circuit.

A. E. WHITE: No installations have been brought to my attention in which the preliminary heating performed with fuel oil is supplemented with electric heating. It is questionable if dual heating of this type will ever meet with favor. In the first place, such dual heating would necessitate increased operating costs as the result of increased handling charges in transferring stock from an oil-fired furnace to an electrically-heated furnace. Presumably one of the outstanding reasons for such a dual system would be the saving in time. This would not appeal to heat treaters. Heat treatment operations should not be hurried. Rapid heating of metal is detrimental to it. Electrically heated furnaces are sufficiently rapid for quality workmanship. For the above reasons, therefore, it would not be advisable to use a dual system.

Drop forgers as a class are desirous of bringing metal to the forging heat in the quickest possible time. Metal is not apt to be materially injured by quick heating in this operation, because the forging operation refines the grain. To date no electric furnaces with a sufficiently rapid rate of heating have been developed. This situation may soon change, as it has been my good fortune to see, with the past few days, an experimental electrically-heated forging furnace which appears to be operating satisfactorily. It seems to be able to heat metal as rapidly as our present oil-fired furnaces.

[9] Head, Division of Electrochemistry, Columbia Univ., New York City.

The plant in which it is installed is in every way pleased with its operation.

C. E. CHANEY[10]: One of the furnaces Prof. White refers to was put into operation last week, and I was a little surprised when I heard him say that it had a "150 per cent efficiency." At the Hudson Motor Car Company you can see that furnace in operation. It is turning out work that is entering at 90° F. (32° C.), coming up to 1350° F. (741° C.) and leaving the furnace at 150° F. (66° C.), and it is doing it at 35 lb. (16 kg.) to the kw.-hr. That is a good deal better than most furnaces can do. In regard to annealing furnaces, Prof. White stated that they were getting 82 per cent efficiency. That is true. There are a good many furnaces of the continuous pusher type which are giving as high as 12.5 lb. (5.7 kg.) per kw.-hr. In these continuous pusher type furnaces it is possible to keep a very low kilowatt demand, and at the same time to put into the furnace a goodly quantity of material in an hour. In other words, by putting in a pound, say, every minute, which would be 60 lb. an hour, the total material is heated up on a much lower kw. consumption that if you put 60 lb. in at once and heated it up in the same hour.

In a new furnace the carburizing pot is held in the furnace from 5 to 8 hours, and after it leaves the heating zone it passes out to another chamber where it heats up the work coming in.

WIRT S. SCOTT[11]: Prof. White refers to the kw.-hr. consumed for industrial heating for one central station. It may be of interest to know that the National Electric Light Association have been trying to collect data from all over the country as to what the industrial heating of the United States is today. They are collecting this information from central stations and manufacturers of electrical apparatus and every available source. We feel we are safe in saying that the industrial heating load in 1923 was 1,250,000 kw. connected; that the load on the central stations is approximately 1,000,000 kw. connected; that this has produced a consumption to central stations of two billion kw. hours for 1923, and that the annual revenue for 1923 for industrial heating was $40,000,000.

A. E. WHITE: Mr. Chaney appears to be somewhat concerned

[10] Holcroft and Company, Detroit, Michigan.
[11] Westinghouse Elec. and Mfg. Co., East Pittsburgh, Pa.

about the statement made to the effect that with a compensating furnace efficiencies of as high as 150 per cent can be procured. This statement at first glance does appear to be ridiculous, inasmuch as we all look upon 100 per cent as the possible maximum value. Let us, however, take Mr. Chaney's own statement to the effect that in one of the compensating furnaces with which he has done work he heats 35 lb. (16 kg.) of metal to 1350° F. (741° C.) with one kw.-hr. It requires 204 B. t. u. to bring a pound of metal to 1300° F. To heat 35 lb. (16 kg.), therefore, would require 7140 B. t. u. One kw.-hr. produces 3415 B. t. u. This would mean, therefore, on the basis of Mr. Chaney's figures, that the furnace to which he makes reference is operating with an efficiency not of 150 per cent, but rather with an efficiency of 209 per cent. Of course, the reason for this high efficiency is found in the fact that because of the compensating principle we are able to use over again heat which has already been employed, and for that reason has been given credit.

A paper presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 3, 1924, Prof. Hirshfeld in the Chair.

ELECTRIC FURNACE FOR CONTINUOUS HARDENING AND TEMPERING WIRE.[1]

By R. H. MacGillivray.[2]

Abstract.

The electric furnace has proven to be an economic factor in hardening and tempering of steel wire, and has been extremely successful. Even distribution of heat throughout the furnace chamber, with absolute control of temperature at the proper point required, insures a uniformly satisfactory product and few or no rejections due to improper heat treatment. The fact that the heat is largely confined in the furnace, and not radiated into the room, has a decided effect in improved working conditions and more efficient and contented work force. Life of the furnace is considerably lengthened, and repairs can be easily and economically made, usually without the necessity of a long shut-down.

In the manufacture of shade roller springs very accurate results are required. The final process, hardening and tempering, must be done under positive control of heating conditions. The wire is a high carbon steel containing in addition a percentage of manganese, silicon, phosphorus and sulfur. This is analyzed very carefully to secure a uniform product.

The old method of heat-treating was done by hardening the wire in cast iron lead pots; the wire was then quenched in an oil bath and drawn in additional lead pots. These pots were heated by producer gas manufactured on the premises.

Results were never fully satisfactory, in that the heating conditions could not be accurately controlled, the actual variation in

[1] Manuscript received July 15, 1924.

[2] Industrial Heating Eng., Westinghouse Electric and Mfg. Company, New York. Experiments carried out for Stewart-Hartshorne Co., East Newark, N. J.

temperature being about ± 15° C., and the further fact that the gas flame burned out the crucibles at least once a month. Incomplete control and distribution of heat by this process resulted in the rejection of large quantities of wire, and the break-down of crucibles, due to burn-out, caused loss of production and material, and also made necessary the labor of rebuilding the furnace.

About one year ago an electric furnace was installed, this being supplied by the Westinghouse Electric and Manufacturing Co. After a short preliminary period of experimenting, this electric furnace more than fulfilled expectations and has been in continuous operation 24 hours a day for the last six months.

This electric furnace consists essentially of two units. One is an electric-heated, air-hardening furnace, approximately 5.48 m. in length (Fig. 1 and 2), the other an electric-heated, lead-drawing pan (under hood in Fig. 3) the quenching being done in oil as heretofore. The hardening furnace has a nickel-chromium retort, with nickel-chromium resistance elements in top and bottom. This retort measures inside 33.02 cm. wide by 6.35 cm. high and 5.48 m. long—the full length of the furnace. Suitable insulation and refractory material surround this retort, filling up the space between the retort and the outer shell of the furnace. The furnace is self-contained and is mounted on a stand, so that if necessary it can be readily moved to some other part of the plant.

The lead-hardening pan rests in an insulated structure similar to the air furnace, but open at the top, with a ventilating hood to remove fumes. The wire is kept immersed in the lead by means of rollers for a distance of about 45.72 cm. of travel.

The process is continuous. From 10 to 32 strands of wire, depending on the size, are run through the air furnace, quenched in oil and drawn through the lead pan. The wire is oval in shape, varying in size from 0.081 cm. x 0.101 cm. to 0.167 cm. x 0.195 cm. The speed of travel ranges from 10.97 to 11.58 m. per minute for the different sizes of wire.

The temperature control is automatic. Each 1.82 m. section of the hardening furnace has separate control, by means of electric pyrometers operating control panels connected on the primary side of automatic transformers. The temperature of the first and second sections is held at 982.2° C. and the exit section at

898.8° C. A recording chart on the pyrometers shows a temperature variation not greater than ± 1.5° C. The lead pan is equipped with a single control of the same design, the temperature being maintained at 376.6° C.

The connected load of the hardening furnace is 61 kw., and of the tempering pan 19 kw. Both operate at comparatively low voltage through 220 v. single phase transformers. Actual tests show an over all operating consumption of 48.5 kw. for both units on continuous production. Power is purchased from a local central station at a sliding scale of rates. The heat-treating department is charged 2 cents per kw-hr. for the furnace operation.

Cost per 100 lb. (45.36 kg.) Finished Wire

	Fuel	Labor and Fuel
Producer Gas Furnace	$0.381	$0.858
Electric Heated Furnace	0.26	0.53

A comparison of costs proves interesting, in that a saving of $0.328 per 100 lb. (45.36 kg.) of wire has been made by installing a modern electric furnace in place of the old gas-heated furnace. Further, the results are uniformly good, with practically no rejections of wire. Time, labor and material are saved, and the furnace in six months' continuous operation has not required any repairs. In this period the gas furnace would have been shut down about nine times for repairs.

The electric furnace occupies less floor space than the gas furnace and has twice the production. Since installing the electric furnace the company has been able to shut down two gas furnaces and still maintain necessary production. The advantages of electric heat are also greatly appreciated by the operators, especially the fact that working conditions are improved, due to the fact that very little heat is released into the room.

DISCUSSION.

WIRT S. SCOTT[3]: With reference to Mr. MacGillivray's paper, I want to say that originally an air-tempering furnace was used. The wire after passing through the hardening furnace is quenched

[3] Westinghouse Elec. and Mfg. Co., East Pittsburgh, Pa.

in oil. It was found that this oil, despite any kind of wiper that was put on the wire, would be carried over into the tempering furnace and that oil on this wire would carbonize, evidently causing a short circuit of the heating elements, and it was necessary in that case to substitute a lead drawing or tempering bath. Regarding lead hardening and lead tempering baths, I think that these offer big possibilities, which have been overlooked in the past. We have a large installation in operation (it is the largest one that our company has installed to date), in which the hardening and tempering is carried out in lead baths, and both baths are heated electrically.

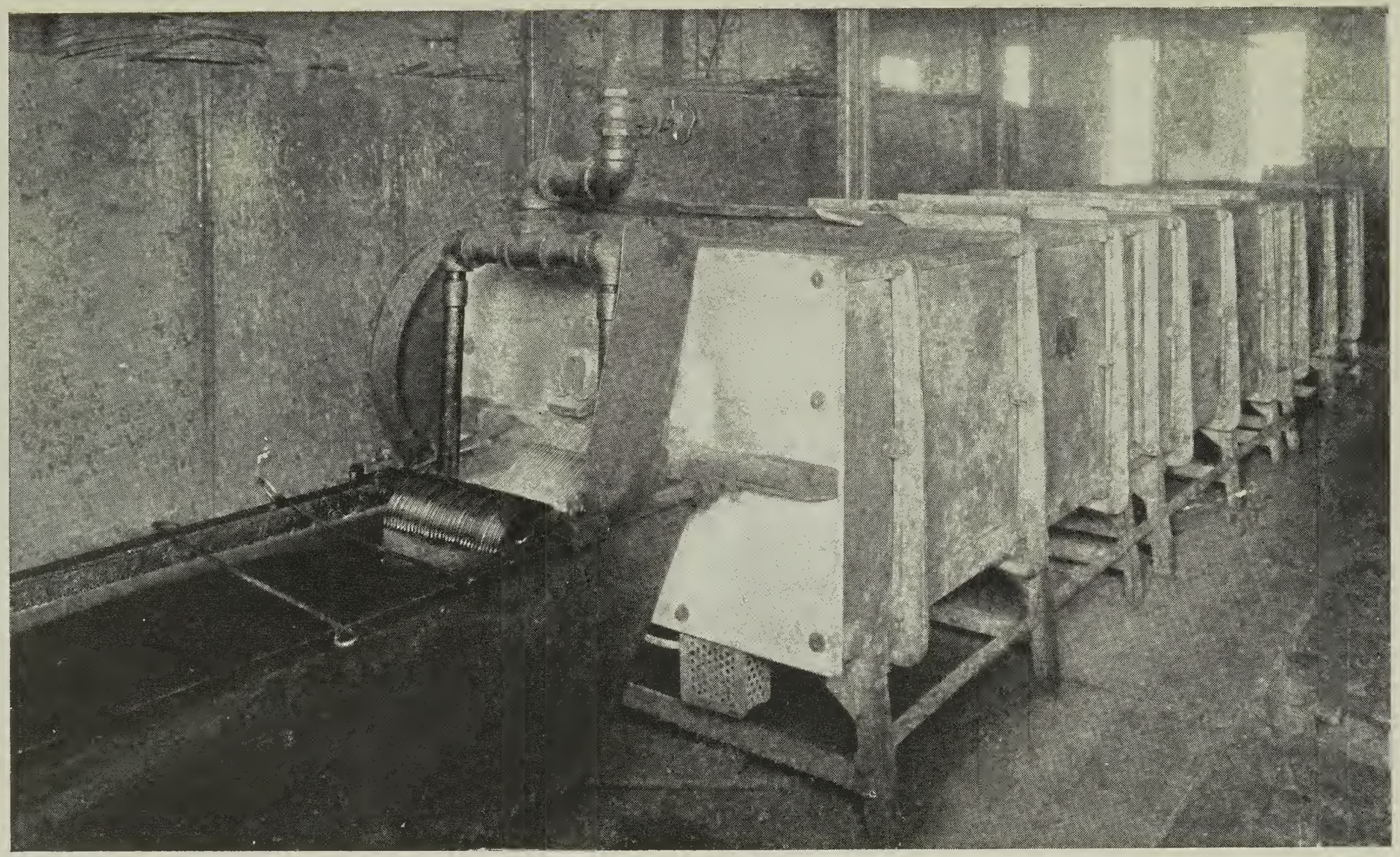


Fig. 1. Showing exit of the electric hardening furnace, with the passage of wire directly into the oil quenching bath.

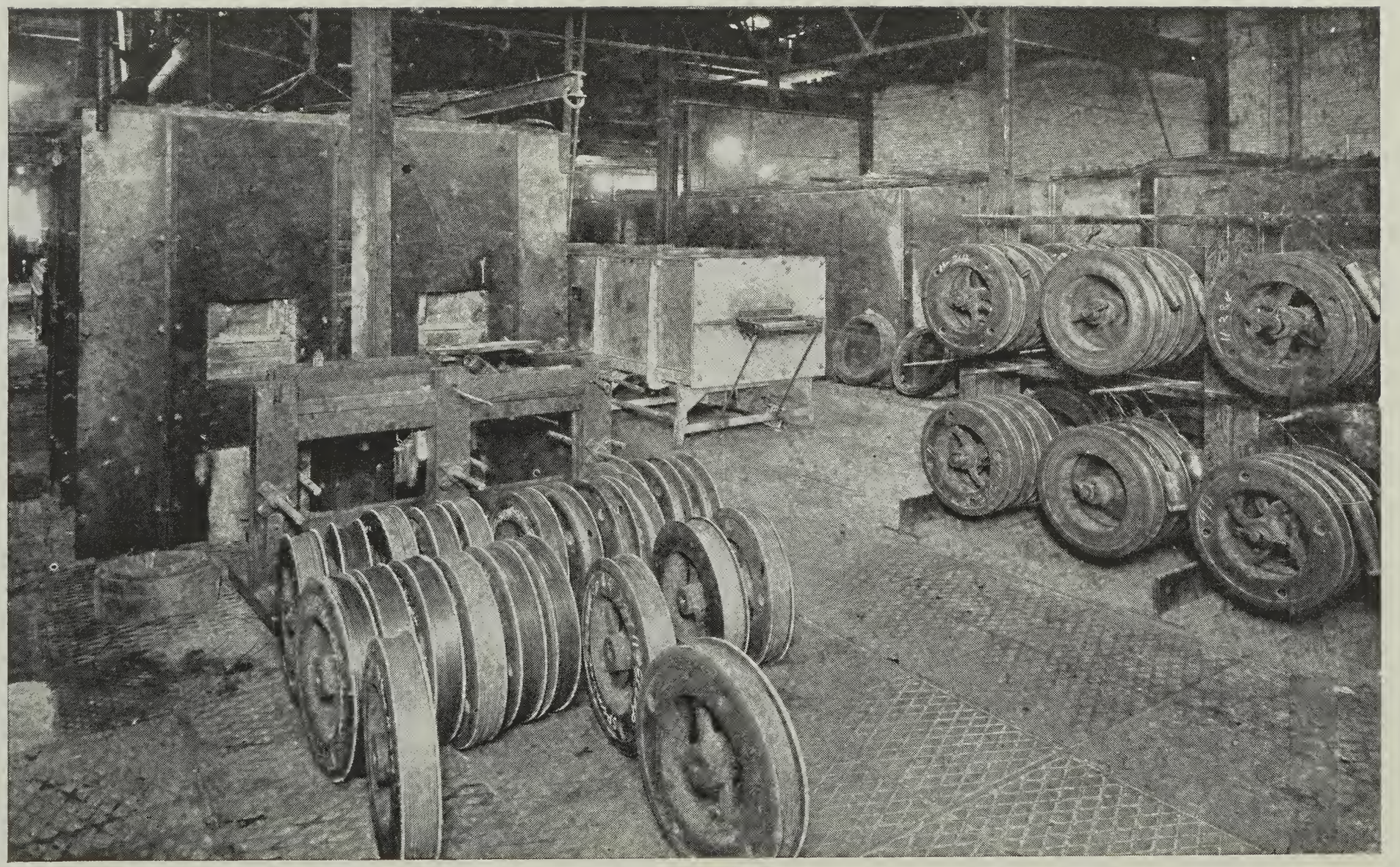


Fig. 2. Showing entrance section of the hardening furnace with 32 strands of wire running from the reels through the furnace. On the left can be seen one of the obsolete gas-fired furn aces, which has been replaced by the electric-heated unit.

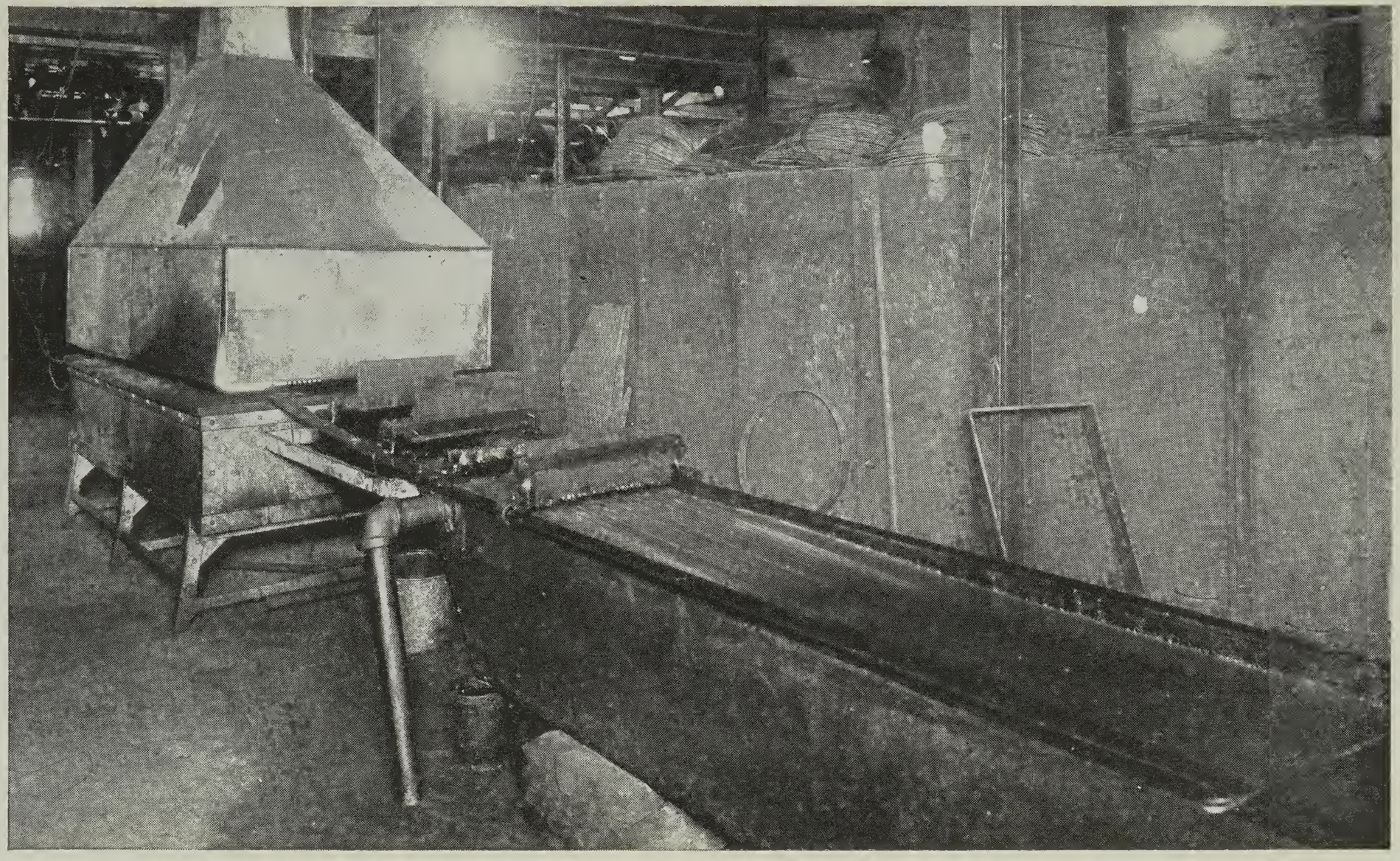


Fig. 3. Lead drawing pan, electrically heated, showing the wire coming from the oil quenching bath and running into the lead furnace. The ventilating stack as shown is necessary to remove all fumes, etc.

A paper presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 3, 1924, Prof. Hirshfeld in the Chair.

ANNEALING OF BRASS TUBING IN THE ELECTRIC FURNACE.[1]

By Robert M. Keeney.[2]

Abstract.

Electric annealing of small brass tubing has proven to be more economical than annealing with wood fuel at the plant of the French Manufacturing Co., Waterbury, Conn. The brass is annealed in a 330-kilowatt electric furnace having inside muffle dimensions of length, 16 ft. (4.88 m.); width, 4 ft. 6 in. (1.37 m.), and height, 18 in. (45.7 cm.). The resistors, consisting of coils made of nickel chromium alloy, are mounted in the walls, roof and floor. With power at 2.33 cents per kilowatt hour and wood at $8.00 per cord, the power cost per ton of brass annealed exceeds the fuel cost by only 7.5 per cent. Yellow brass tubing in small sizes, and thin gauges can be annealed with a power consumption of 110 kilowatt hours per ton (2,000 lb.; 907.2 kg.) of tubing, or 18.2 lb. (8.05 kg.) per kilowatt hour. Lower labor costs due to greater rate of production, less time required for pickling because of much less oxidation of the brass, and no handling of wood, result in lower total costs for electric annealing.

Electric furnace annealing of light-weight brass tubing has made such progress during the past five years that it probably will gradually replace combustion furnace annealing, particularly in mills drawing seamless tubing in small sizes and thin gauges. In the early days of the brass industry tubing was always annealed in wood-fired muffle furnaces. Although oil-fired furnaces are now largely used on heavy tubing, many tubing manufacturers still use wood-fired muffles, because the practice has been established for

[1] Manuscript received July 15, 1924.

[2] Industrial Heating Engineer, Westinghouse Electric and Mfg. Co., Boston, Mass.

years, and because of the mild heat obtainable in the combustion of wood.

In large centers of the brass industry, such as the Naugatuck Valley of Connecticut, the use of wood for heating annealing furnaces during the past 100 years, and the demands of modern industry for wood for more constructive purposes, have resulted in a heavy depletion of the adjacent forests, and a consequent increase in the cost of wood. With the fuel cost constantly increasing and central station power costs gradually decreasing, electric heat seems to be the ideal method of heating for the mill which wishes to provide ideal working conditions for its employees, and wishes to eliminate the labor and uncertainty involved in maintaining a fuel supply. This applies particularly to the concern of moderate size, which simply draws tubing. City gas has proven both expensive and objectionable, and the quantity of gas involved is usually not sufficiently large to warrant the installation of a producer gas plant with the addition of another operating department to the plant. Oil does not seem to appeal to the manufacturer of small tubing, as the lower fuel cost does not offset its disadvantages.

Another factor to be considered is the class of labor employed in a seamless tube mill. Many of the employees have been working for the same mill for many years. The tube mills are located in the same room with the annealing furnaces. To keep these skilled employees contented, and to prevent the heavy loss due to labor turnover, the more progressive and far-sighted manufacturer realizes that the best possible working conditions must be provided. The electric furnace does this, with the elimination of all gases and oil, and results in a much cooler room. Thus, as in all modern industry, the trend is toward electric heat.

ELECTRIC ANNEALING OF BRASS AT THE PLANT OF THE FRENCH MANUFACTURING CO.

Wood-Fired Muffle.

The French Manufacturing Co., of Waterbury, Connecticut, manufacturers of seamless brass and copper tubing in small sizes, and thin gauges, have recently placed in operation a 330-kilowatt electric muffle furnace, after a careful investigation of operating costs and the metallurgical results to be obtained by the use of

electric heat. The electric furnace has replaced a wood-fired muffle furnace, now dismantled, which had inside muffle dimensions of length, 16 ft. (4.88 m.); width, 4 ft. (1.22 m.), and height to spring line of arch 18 in. (45.7 cm.). There were two fire boxes on one side of the muffle, from which the products of combustion passed over the charge, down through flues on the side opposite to the fire box, under the floor, and out to the stack located on the same side as the fire box. The tubing was loaded into U-shaped racks, 12 in. (30.5 cm.) wide by 12 to 16 in. (30.5 to 40.7 cm.) high, which were loaded onto a pan about 15 feet (4.58 m.) long by 3 ft. 6 in. (1.07 m.) wide, the pan weighing 400 lb. (181.4 kg.). The weight of charge, varied from 1,000 lb.) 453.6 kg.) to 3,000 lb. (1,360.8 kg.). Six cast iron rails supported the pan in the furnace. The furnace was operated at a temperature of 1,200° F. (648° C.). It required 2 hours in the morning to attain this temperature, and the length of time a charge was heated varied from 45 minutes to two hours. A load of tubing, 0.3125 in. (7.9 mm.) outside diameter and 0.028 in. (0.71 mm.) gauge, weighing 1,189 lb. (540 kg.), was annealed in one hour. The load was 36 in. (91.5 cm.) wide, 9 in. (22.8 cm.) high by 13 ft. (3.96 m.) long.

Rate of Heat Penetration

The electric resistance of the muffle type has one characteristic in common with the fuel-fired muffle furnace for annealing brass tubing, in that it is not practical to attempt to heat each brass tube to the same temperature, because of the slow rate of heat penetration through brass tubing in a muffle furnace of any type, if the tubing is piled to a practical height. This has resulted in considerable experimentation by several brass manufacturers on the heating of individual tubes by passing current through the tube itself, that is, the tube acts as a resistor. However, brass tubing may be annealed within a rather wide range of temperature, from 1,000° to 1,350° F. (538° to 732° C.). In a general way this was apparent from observation of the wood-fired muffle, in which there were obviously tubes higher than 1,200° F. (648° C.), and much of the brass was at a lower temperature.

Experiments were conducted in an electric furnace by annealing the brass at various temperatures followed by testing its drawing

qualities. These tests demonstrated that tubing annealed at 1,000° F. (538° C.) would draw satisfactorily and that tubing heated to 1,350° F. (732° C.) was not burned. The experiments determined the temperature to which the center of the charge should be heated, or the last part of the charge to be heated, as 1,000° F. (538° C.), and the temperature of the muffle as 1,350° to 1,400° F. (732° to 760° C.) maximum.

A second series of experiments was conducted to determine the rate of heat penetration in the electric furnace with varying muffle temperatures, but with the brass piled as in wood-fired furnace practice. The furnace used was of the radiant type with exposed heating elements. There were heating elements in the floor, beneath the alloy floor plates, on the side walls and in the roof. The inside muffle dimensions were: length, 6 ft. (1.83 m.); width, 32 in. (81.3 cm.), and height to spring line of arch, 16 in. (40.7 cm.). The rated capacity was 81 kilowatts. In each experiment the charge consisted of yellow brass tubing, 0.3125 in. (7.9 mm.) diameter, 0.028 in. (0.71 mm.) gauge, by 5 ft. 2 in. (157.5 cm.) long, piled 11 in. (27.9 cm.) high and 15 in. (38.1 cm.) wide, and resting directly on the floor plates. The results of two charges are shown in Table I. In Experiment No. 1 the muffle temperature was maintained at 1,120° F. (605° C.), and the furnace was saturated at this muffle temperature before the tubing was charged. A thermocouple was placed in the center of the charge about 2 ft. (61 cm.) back from the front end. In Experiment No. 2 the muffle temperature was 1,400° F. (760° C.). In addition to the thermocouple inserted in the charge as in Experiment No. 1 another thermocouple was placed on top of the charge, to ascertain the temperature at this point, and check it up with the condition of the brass in respect to overheating.

Experiment No. 1 represents ideal but impractical conditions. All of the brass has been annealed at about the same temperature, 1,100° F. (593° C.). The rate of penetration is so slow that output would be reduced to such an extent as to make capital charges prohibitive. The rate of penetration was 2 in. (5.1 cm.) per hour, to a center of charge temperature of 1,000° F. (538° C.) and with a furnace temperature of 1,120° F. (605° C.). In Experiment No. 2 the rate of penetration was 4.1 in. (10.4 cm.)

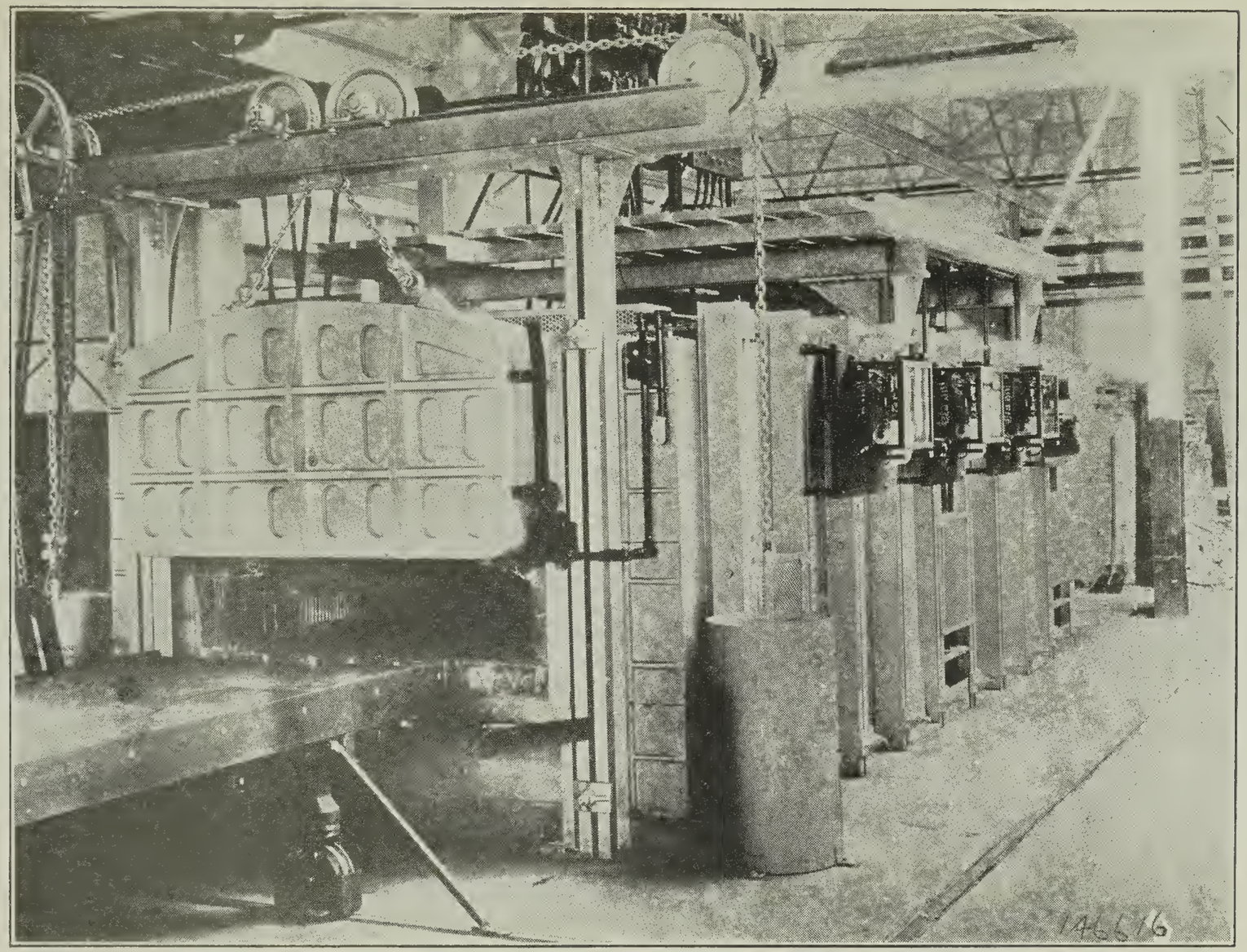


Fig. 1. Front view of electric furnace for annealing brass tubing at the plant of the French Mfg. Co., Waterbury, Conn.

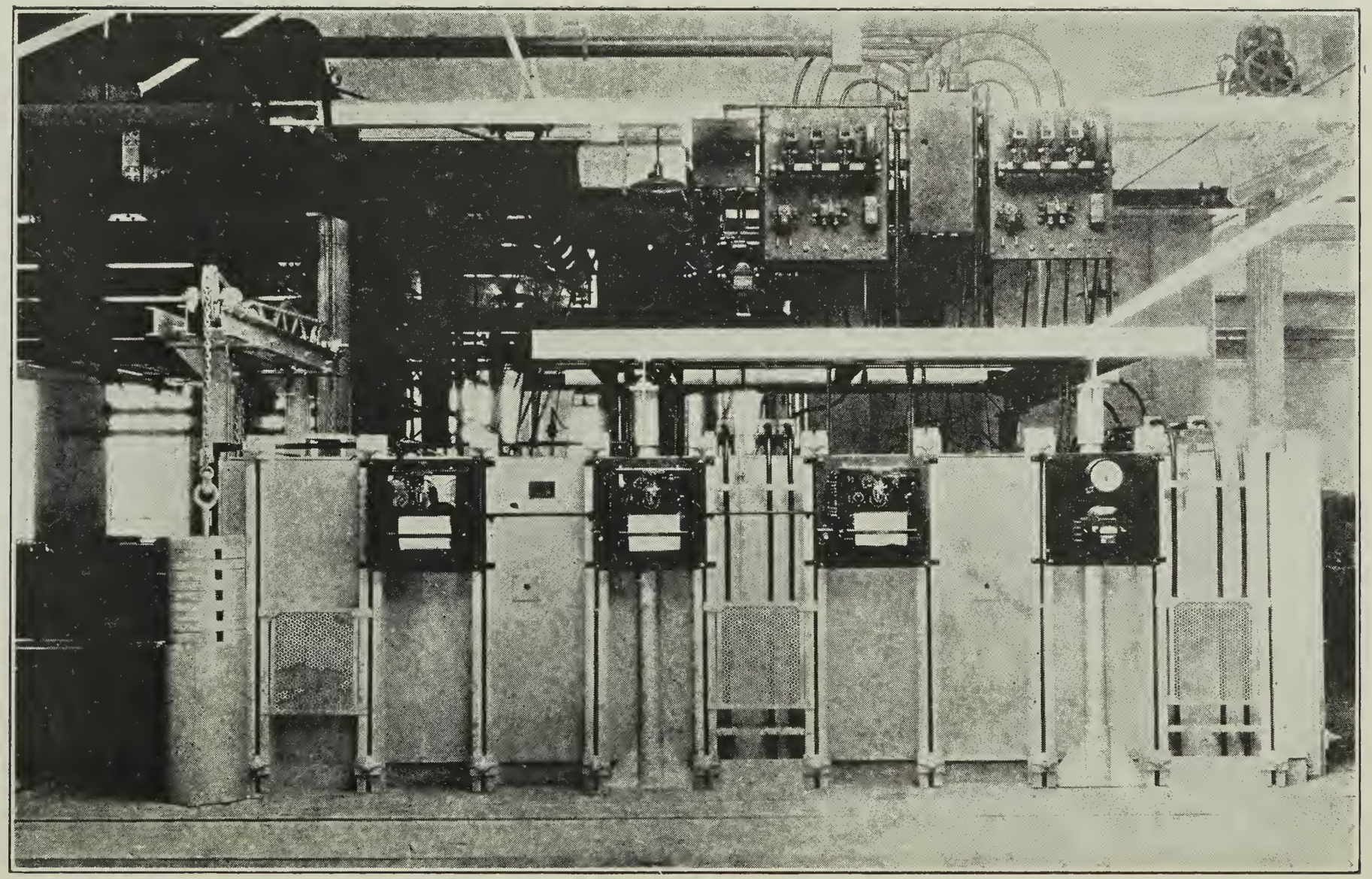


Fig. 2. Side view of electric furnace for annealing brass tubing with automatic temperature control equipment on side and on top of furnace.

per hour with a center of charge temperature of 1,100° F. (593° C.) and a furnace temperature of 1,400° F. (760° C.) and the temperature of the outside of the charge, 1,345° F. (730° C.). Experiment No. 2 indicated that for commercial operation the proper compromise with ideal conditions could be obtained by raising the muffle temperature to the maximum commensurate with an unburned brass, and lowering the depth of charge by widening the muffle.

TABLE I.

Rate of Heat Penetration.

Temperature of muffle in Exp. No. 1, 1120° F. (605° C.); in Exp. No. 2, 1400° F. (760° C.)

Time		Experiment No. 1 Center of Charge		Experiment No. 2			
				Center of Charge		Top of Charge	
hr.	min.	° F.	° C.	° F.	° C.	° F.	° C.
..	0	70	21	70	21	1230	665
..	10	70	21	90	32	1295	702
..	30	130	55	220	105	1325	718
..	40	200	94	395	202	1335	723
..	50	290	143	605	318	1340	727
1	0	475	247	795	422	1345	730
1	10	620	328	965	518	1345	730
1	20	695	369	1100	593	1345	730
1	30	800	427	1200	648	1345	730
1	40	925	496				
2	0	1025	552				
2	15	1065	573				
2	25	1090	588				
2	35	1095	591				
2	40	1100	593				

As a result of these experiments it was clearly demonstrated that the electric muffle furnace will not give any more uniformly annealed charge than the combustion furnace unless production is sacrificed to ideal conditions, with the exception that, due to automatic temperature regulation, the upper limit of temperature can be controlled so as to prevent burning of the brass. In all the experiments made it was evident that there was less oxidation of the brass than in the wood-fired muffle, a conclusion subsequently confirmed in commercial operation.

Electric Furnace.

The 330-kilowatt electric furnace, Fig. 1 and Fig. 2, has inside muffle dimensions of length, 16 ft. (4.88 m.); width, 4 ft. 6 in. (1.37 m.); height to spring line of arch, 18 in. (45.7 cm.), and height of crown of arch, 22.5 in. (57.1 cm.). At the front end there is a vestibule 18 in. (45.7 cm.) deep in addition to the 16 ft. (4.88 m.) of length. The vestibule has a door opening with width, 4 ft. 6 in. (1.37 m.), and height to spring line of arch, 12 in. (30.5 cm.). The furnace is insulated with 16 in. (40.7 cm.) of moulded Celite brick. It occupies a floor space 10 ft. (3.05 m.) wide and 21 ft. (6.4 m.) long.

Open radiant coils are mounted in the walls, roof and floor, the

bottom coils being covered by alloy floor plates, which in turn support the alloy rails on which steel pans holding the charge are moved in and out of the furnace, by a motor-driven charging device. There are 36 coils in the furnace, divided as follows: 16 coils in the roof, 4 coils in each side, and 12 coils in the floor.

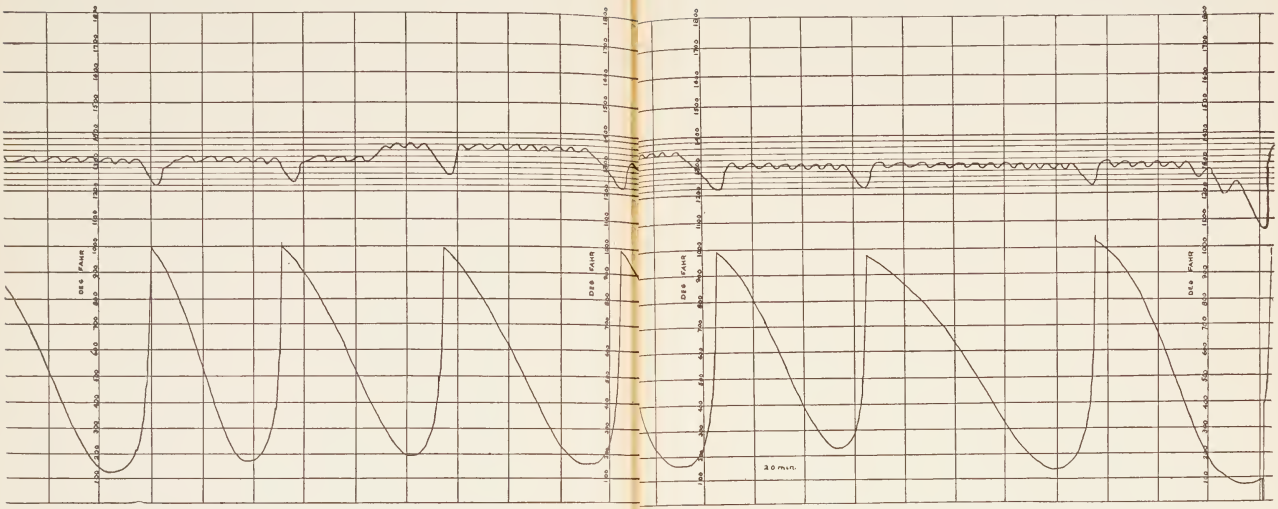


Fig. 3. Temperature chart of electric furnace in operation. The upper curve represents the automatic control of the front section, and the lower curve the temperature of the charge. The time between each vertical line is 20 minutes.

All coils are interchangeable throughout and are made of No. 1 B. & S. gauge chromel A wire, 0.289 in. (7.34 mm.) diameter. Chromel A alloy consists of approximately 78 per cent nickel and 19 per cent chromium, with iron, manganese and silicon as impurities.

The coils are divided into two control circuits, each 18 ft. (5.49 m.) long and covering one-half the length of the muffle.

The connected load of each circuit is 165 kilowatts. Each group is controlled automatically by a Leeds and Northrup recording control pyrometer and a 3-pole 600-ampere contactor panel. The furnace operates on 230-volt, 3-phase, 60-cycle circuit, with the coils in each group giving a balanced 3-phase load. The contactor panels are mounted on pipe frames over the furnace, and the control pyrometers on the buckstays of the furnace. In addition to the Leeds and Northrup controllers there is a high temperature protective cut-out in each circuit, which cuts off the power in case of overheating due to failure of the automatic control.

Operation of the Furnace.

In the operation of the furnace all chance has been removed from the annealing process by automatic control, not only of the muffle temperature, but also control of the temperature of the charge itself. The muffle temperature is varied from 1,200° to 1,350° F. (648° to 732° C.), depending on the gauge of the tubing, a lower temperature being used on thin tubes. The temperature of the center of each charge is recorded by a Leeds and Northrup recording pyrometer, the thermocouple of which is inserted through a hole in the door into a pipe which has been set in the end of the charge in the vertical center of the mass. The charge is withdrawn when the recording pyrometer indicates a temperature of 1,000° F. (538° C.), as shown in Fig. 3, the top curve representing the automatic control of the front section, and the lower curve the temperature of the charge.

The charge is loaded in U-shaped racks, 15 in. (38.2 cm.) wide by 10 in. (25.4 cm.) high to a depth of about 7 in. (19.8 cm.), and placed on a steel pan 16 ft. (4.88 m.) long by 4 ft. (1.22 m.) wide, four rows of racks per pan. To secure the highest efficiency the pans are loaded full on each charge if possible. The pans are brought to the furnace on table trucks, and pushed into the muffle by the motor-driven charger. When the recording pyrometer indicates a temperature of 1,000° F. (538° C.) at the center of the charge, that is, the vertical center, the charge is pulled and after cooling a little is pickled in acid.

Depending largely on the weight, the time per charge varies from 45 to 80 minutes. Ten to twelve charges of 2,000 to 3,000 lb. (907.2 to 1,360.8 kg.) of brass per charge are annealed per

10-hour day, including the charge left in the furnace during the night. The furnace cools from 1,300° F. (705° C.) to 1,050° F. (565° C.) after a nightly shut-down with a cold charge inserted after the last charge of the previous day has been drawn, and the circuit opened. After a weekly shut-down, from Saturday noon until Monday morning, it cools to a temperature of 900° F. (482° C.). On weekday mornings 1,300° F. (705° C.) is regained in 30 minutes, with the charge annealed during the night still in the furnace. On Monday the muffle temperature reaches 1,300° F. (705° C.) in 45 minutes. When a charge has been drawn, the temperature of the muffle drops from 1,300° (705° C.) to 1,200 to 1,240° F. (648 to 672° C.), but regains 1,300° F. (705° C.) within 10 to 15 minutes after the next load has been charged. Charging and discharging require two minutes.

The electric furnace has exceeded the estimated production figures. The power consumption averages 110 kw.-hr. per ton (2,000 lb.) (907.2 kg.) of brass annealed, or a production of 18.2 lb. (8.25 kg.) of brass per kilowatt hour, as compared with an estimated production of 16.2 lb. (7.34 kg.) per kilowatt hour. With power at 2.33 cents per kilowatt hour, and with wood at $8.00 per cord, the power cost per ton of brass annealed exceeds wood cost per ton of brass annealed by only 7.5 per cent, with no labor for handling wood included. There is considerably less oxidation of brass in electric furnace annealing, so that the pickling time has been reduced by at least one-half with a corresponding reduction in acid consumption. Over a period of years an increase in brass inventory will undoubtedly result.

The electric furnace is operated with one or two men per 10-hour day less than the fuel furnace, and the number of pickling tubs in use has been reduced from four to two. One man per day, formerly used in handling wood, has been eliminated. The working conditions in the shop have been much improved. The brass annealing operation is now conducted free from the variations resulting from the human element, but with a heat as mild as can be obtained in the wood-fired muffle, conditions which are certain to produce a more uniform product. The success of the electric muffle has led to the electrification of two gas-fired bright annealing furnaces by the French Mfg. Co. In brief, under the conditions existing at this plant electric brass annealing is not

only a cleaner and more easily conducted operation than wood-fired annealing, but it is also a less costly method of annealing brass tubing.

CONCLUSIONS.

1. Under the conditions outlined above, electric brass annealing is more economical than annealing with wood fuel.

2. With power at 2.33 cents per kw.-hr. and wood at $8.00 per cord, the power cost per ton of brass annealed exceeds the fuel cost by only 7.5 per cent.

3. Yellow brass tubing in small sizes and thin gauges can be annealed with a power consumption of 110 kilowatt hours per ton (2,000 lb.) (907.2 kg.) of tubing, or a production of 18.2 lb. (8.25 kg.) per kilowatt hour.

4. Although all of the tubes being annealed in an electric muffle will not be annealed at the same temperature unless production is sacrificed to ideal conditions, just as in the wood-fired furnace, the removal of the human element by the automatic control of the electric furnace eliminates chance in the operation and results in a more uniform product than that of the wood-fired muffle.

5. If the scale of production warrants automatic charging, the electric furnace annealing of tubing can be made a completely automatic operation.

6. For the purpose of drawing, annealing at from 1,000° F. (538° C.) to 1,350° F. (732° C.) gives satisfactory results.

7. There is much less oxidation of brass when annealed in the electric muffle furnace than when annealed in the wood-fired muffle, resulting over a period of years in an increase in the brass inventory.

8. The pickling time is reduced by at least one-half, with a corresponding reduction in acid consumption and in the number of pickling tubs.

9. The labor costs are reduced more than sufficiently to offset the slightly greater cost of electric heat over wood cost, and the increase of capital charges.

10. The working conditions in the shop are much improved, with labor more contented and less labor turnover.

Acknowledgment is made of the broad-minded policy of F. W. French, president of the French Manufacturing Co., in giving permission to publish the information contained in this paper.

DISCUSSION.

WIRT S. SCOTT[3]: There is a furnace in Newark for annealing copper wire. It is a continuous process furnace. The wire enters the furnace under a water seal and leaves under a water seal. There is no objection to the hot material coming out of the water in the case of brass or copper. The furnace is electric.

E. F. COLLINS[4]: Concerning the treatment of non-ferrous metals, especially copper, in the electric furnace, what has been said refers largely to the annealing of copper without consideration for the use to which such copper is to be put.

It may be desirable to anneal copper without oxidation, and again for other purposes it may be necessary to anneal copper in an oxidizing atmosphere. Of course, where copper is annealed in an oxidizing atmosphere there does not seem to be any special advantage to carry on this process in the electric furnace, and there are many cases in which these conditions are required by various manufacturers. Hence, it would seem that fuel-fired furnaces are entirely suited for this purpose.

However, when non-oxidizing conditions are desired and a bright anneal of copper is the object, then the electric furnace is to be preferred. As a matter of fact, it has been found that copper annealed in an electric furnace, fitted with water-seals, gives a very high quality of anneal. A degree of ductility and softness is found in copper treated by this method that has not been obtained in the fuel-fired furnace, even when it has been fitted with a muffle and water-seal. The reason for this is not clear, but these are the facts that have been arrived at as the result of many tests and observations.

A. E. WHITE[5]: I have listened with much interest to what has been said with regard to the brass industry. A few years ago

[3] Westinghouse Elec. and Mfg. Co., East Pittsburgh, Pa.
[4] Consulting Engr., Industrial Heating Dept., General Electric Co., Schenectady, N. Y.
[5] Director, Dept. of Engineering Research, Univ. of Michigan, Ann Arbor, Mich.

the industry was in just about the state set forth. Last Friday, when I was in Waterbury, however, it was my good pleasure to learn that in one plant 40 electric furnaces were engaged in the melting of brass products. This same plant also employed a Snead Electric Annealer for the finish anneal for brass tubing. This method of annealing appears to have many valuable applications for metal of uniform cross section. As you quite appreciate, the principle involved calls for the annealing of metal by the heating effect resulting from the resistance of the metal to the passage of electric current.

A paper presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 3, 1924, Prof. Hirshfeld in the Chair.

ELECTRIC FURNACE PRACTICE IN THE BRONZE FOUNDRY.[1]

By F. C. Heath.[2]

Abstract.

The foundry described is located in Detroit, Mich., and has installed 5 Detroit electric furnaces. These furnaces are of the indirect arc, rocking type. The charge weighs 104 kg. The furnaces are equipped each with a 100 k. v. a. transformer, operating at an average rate of input of 90 to 100 kw. Each furnace makes 21 heats per day, the average time of melting being 17 min., with a loading and unloading time of 6 min., making a total of 23 min. for the complete cycle. The best record for coke fires and crucibles is a melting time of 75 min. The linings of the electric furnaces are renewed about every 1,000 heats. The energy consumption amounts to 325 kw.-hr. per ton of bronze, and 6.5 lb. of electrodes per ton. The bronzes manufactured are chiefly 88 Cu, 10 Zn, 2 Sn; 80 Cu, 10 Zn, 10 Sn; 85 Cu, 5 Zn, 5 Sn, 5 Pb; and 85 Cu, 5 Zn, 9 Sn, 1 Pb. The saving in cost, compared with coke-crucible practice, amounts to about $3.00 per ton. [C. G. F.]

The greatest potential field for the electric furnace is in the medium-sized foundry. In such foundries melting, molding, pouring and shaking out is a continuous process, with all these operations going on at the same time. I will venture to say that any one of our molders will have no more than 16 molds standing at any one time, and from 8 to 12 of these will just have been poured. This means that our tonnage of 23,000 lb. (10,909 kg.) per day is poured with the minimum amount of molding space. This

[1] Manuscript received September 22, 1924.

[2] Chief Engineer, Federal-Mogul Corp., Detroit, Mich.

condition requires a small furnace to preserve the flexibility of the coke fires. In fact, the small 250-lb. (110-kg.) furnace is more flexible than the coke fires, since it is necessary to wait no longer than half an hour if a quick change in the melting program is found imperative, as frequently occurs in our line of business. We melt probably 15 different bronzes, although no more than 5 or 6 are run in any one day. This, also, requires flexibility.

We are operating at the present time 5 Detroit Electric Furnace Company's rocking type furnaces, melting 230 lb. (104 kg.) to the charge, or the capacity of a No. 70 crucible. These furnaces are equipped each with its own 100 k.v.a. Kuhlman transformer, operating at an average rate of input of 90 to 100 kw. We originally were equipped with 60 k.v.a. transformers, and produced around 12 to 15 heats per furnace per day. We soon found that brass could be melted much faster, and then changed to the 100 k.v.a. transformer to have plenty of capacity, and our record now stands at 21 heats in one day from one furnace, starting the arc at 6.15 A. M. and finishing the 21st heat at 3.15 P. M.

After the first 2 or 3 heats, which always take more energy than the succeeding heats, the average time of melting was 17 minutes, with a loading and unloading time of 6 minutes, making a total of 23 minutes for the complete cycle. I think I am safe in saying that this is the quickest time that any bronze has ever been melted in production.

The greatest number of heats that I know of being taken out of any one of our coke fires in a day is 6, with a melting time of from 1¼ to 1½ hours. So far, our limiting factor in the speed of melting is the lining. The quality of the bronze is unimpaired by the quick melting, as I will show later. (See Table II.)

The operating advantages are: (1) The human element is largely eliminated and the field for obtaining labor widened; (2) greater uniformity of product, each heat being melted under the same conditions as every other heat as nearly as it is possible to do; (3) the use of the crucible is eliminated, except for carrying metal from the furnace to the molds; (4) everything put into the furnace is melted and taken out, with the resultant low metal loss, according to our two days' test, of 0.6 per cent.

With coke fires, some of the metal is liable to spill out into the

coke while charging; pots sometimes leak and sometimes burst in the fire. Foundries vary in their estimate of loss in the coke fire, but in a test that we ran, without any of the accidents which I have enumerated happening, we found a melting loss of 2 per cent.

As I have mentioned previously, linings are the limiting factor in melting. With the rate of imput of 75 kw. we had a lining last 2,000 heats, but with the rate of input of 90 to 100 kw., it is not economical to run the lining over 1,000 heats.

The average consumption of electricity per ton for our class of bronzes is 325 kw. hr., with an electrode consumption of 6.5 lb. (3 kg.) per ton. We melt principally bronzes of the composisions shown in Table I.

TABLE I.

No.	Copper Per Cent	Tin Per Cent	Lead Per Cent	Zinc Per Cent
1	85	5	5	5
2	85	5	9	1
3	80	10	10	..
4	88	10	..	2

Table II below gives some tests we have made of the physical properties of coke and electrical-fired furnaces on metal analyzing 85 per cent copper, 5 per cent each of tin, lead and zinc.

TABLE II.

Physical Properties of Bronzes.

Type of Furnace	Coke Fired	Electric	
Melting Time	75 min.	17 min.	25 min.
Elastic limit, lb. per sq. in.....	15,560	16,560	16,610
Elastic limit, kg. per sq. cm.....	1,094	1,164	1,168
Ultimate strength, lb. per sq. in...	30,900	30,620	28,940
Ultimate strength, kg. per sq. cm..	2,172	2,153	2,035
Elongation in 5 cm., per cent.....	17	17	18.5

These tests prove that the quality of metal in either process is equally good, and that fast melting in the electric furnace does not injure the metal.

COMPARATIVE COSTS.

So far as the comparative cost of melting is concerned, as near as I can estimate there is about $3.00 per short ton (910 kg.) of melt in favor of the electric melting with our equipment. This is an estimate, as we are still running coke and electric fires with the same operators, and it is difficult to keep separate records. However, we feel that this is accurate at the present prices of coke, electricity, crucibles, etc. Details of the cost are given in Table III.

TABLE III.

Comparative Costs. Per Short Ton (910 kg.)

Coke Fires		Electric Furnace	
Coke at $8.00 per ton	$5.20	Electric Power	$6.50
Crucibles	2.10	Electrodes	1.69
Wood	0.30	Linings	0.56
Charcoal	0.30	Charcoal	0.30
Repairs on Linings	0.90	Repairs on Linings	0.20
Metal Loss, 3 per cent	5.20	Metal Loss, 0.6 per cent	1.80
Labor	0.50	Labor	0.32
	$14.50		$11.37

DISCUSSION.

G. K. ELLIOTT[3]: The feature which appeals to me in this interesting paper, on which I congratulate the author, is the speed of melting. At the Round Table held by this Society a year ago, at Dayton, considerable fear was expressed as to the possible effect on metals by rapid melting, and that may have been the inspiration for this part of the present paper. I am not surprised to see that Mr. Heath's data do not indicate that the metal is materially injured. A parallel is the rapid electric melting of steel, which has become so common in electric steel foundries. It has never been as yet discovered that speedy melting has any particularly deleterious effect upon steel castings. Within the last year I have heard that there has been introduced into one or two brass foundries a rapid melting process, involving the use of high pressure

[3] Chief Chem. and Met., Lunkenheimer Co., Cincinnati, Ohio.

oil, whereby charges of 500 lb. are melted down in from 10 to 20 minutes, and at the time it struck me that this is going to be a serious competitor of the electric furnace, because this rapid melting with oil materially cuts down the fuel consumption. I have not had a chance to compare costs, but I am impressed with the fact that here are an oil furnace and an electric furnace both featuring speed in melting.

F. A. J. FitzGerald[4]: An interesting point in Mr. Heath's paper is the life of his linings. When melting at the lower rate his linings lasted 2,000 heats, and at a higher speed of melting 1,000 heats. It would be interesting to those who are studying refractories to know just how the linings fail. How does the melter know when he needs a new lining? Is failure due to high temperature which causes the melting down of the refractories?

F. C. Heath: It is not due to the breaking down or melting of the linings; it is because the linings have the tendency to crack and then the metal runs into these cracks and destroys your insulation. It is a question of determining in advance the best time to take the lining out. As the lining grows older, the kilowatt consumption increases.

H. M. St. John[5]: I believe that any discussion of melting speed is incomplete unless mixing of the charge during melting is also mentioned. I doubt that a charge of brass can be melted in 17 minutes with good results, unless some means are employed to thoroughly mix the metal during melting, or it might be better to say, some means to "mix the heat with the metal." Mixing the metal is of less importance than the rapid distribution of heat to all parts of the metal in the charge. Otherwise such a high rate of melting is going to mean that the surface metal gets exceedingly hot, while metal nearer the bottom is decidedly colder. I question whether injury to the metal would not result under these conditions. If this is true, it means that the faster you melt, the faster you must mix. It is conceivable that if you mix the metal rapidly enough you could safely melt a charge in one or two minutes.

With reference to the furnace lining, it has always been my experience that linings in this type of furnace fail, as Mr. Heath

[4] FitzGerald Labs., Niagara Falls, N. Y.
[5] Chief Metallurgist, Detroit Lubricator Co., Detroit, Mich.

says, by cracking. If you run a lining to the end of its mechanical life, regardless of heat economy, you will eventually have to shut down because portions of the lining have cracked out completely. Furthermore, molten metal will penetrate the lining and burn its way through the outer steel shell. A lining which would stand this type of service without spalling or permitting metal penetration through the joints would last almost indefinitely.

J. A. SEEDE[6]: Mr. St. John has brought out a very important point about the Detroit furnace; that is, if the furnace did not agitate the metal it would not be melted as rapidly as Mr. Heath has stated. I have seen an experimental furnace of another type where the arc was perhaps a foot above the stationary metal and with zinc fumes boiling off furiously, and at, say, perhaps 9 or 10 in. (23-25 cm.) below the surface there would be cold brass chips. I am much interested in Mr. Heath's paper, and I would like to ask him if he would tell us how many days' operation 1,000 heats mean.

F. C. HEATH: Probably our average would be around 17 heats a day. It is governed largely by the production demands. We run faster on some days than on others. Accordingly, 1,000 heats would mean about two months or more.

J. A. SEEDE: There was another question. This 0.6 per cent loss that you had, is that zinc, or is that of the whole metal?

F. C. HEATH: I did not determine that. The analysis of the metal showed it to be correct. That is all I can tell you.

J. A. SEEDE: That will include spills, etc?

F. C. HEATH: Yes, it was taken right from the weight of charge in the furnace.

[6] Electrical Engr., General Electric Co., Schenectady, N. Y.

A paper presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 3, 1924, Prof. Hirshfeld in the Chair.

ELECTRIC JAPANNING.[1]

By Harry Allen.[2]

Abstract.

The following is a brief review of the development of electrically heated enameling ovens, and the progress made in the art of enameling automobile parts at the Dodge motor car plant. With the co-operation of the different manufacturers, whose product is used, experimental work has been carried on to the end that steady improvement has been made in meeting the requirements of production on a large scale, in the quality of enameled work, economy in baking time, and in bettering the working conditions in these departments. The results secured at present are obtained with the utmost dependability, and are accomplished by labor which is easily replaced. As less than a single day's production of sets of enameled parts is carried in stock, it is essential that the enameling department be able to produce high-quality work every day in the year, regardless of weather conditions.

OVENS FOR OPEN-MODEL BODIES.

In December, 1914, enameling was done for the first time in 15 box-type direct-fired ovens. These were used for enameling bodies, open-model type, and had a capacity of four bodies each. The time of bake was four hours, and as the production increased they were operated day and night. The output of the plant was increasing rapidly, and it was evident that radical changes would be necessary in the enameling department to keep step with the rest of the plant. As there was no room for the addition of simi-

[1] Manuscript received Oct. 4, 1924.
[2] Dodge Motor Car Co., Detroit, Mich.

lar oven units, it was decided to do some experimental work, which would have for its object the determination of the best enamel and correct temperature for the shortest time of bake, maintaining however the high quality of the finished product. A brick and plaster oven was constructed, amply large to hold one body. In order that uniform heating conditions might be had over a wide range of temperatures, electric heaters were installed.

Co-operating with the enamel manufacturers, sufficient test data were obtained to show that a considerable saving in time of bake was possible, and that there were many advantages in the use of electricity for heating. After the prejudices against the use of electricity for this purpose, prevalent at that time, had been overcome, it was definitely decided to equip the ovens with electric heaters. However, the gas ovens were not suitably constructed for this application, and confronted with the prospect of building new ovens, our engineers went one step further and designed conveyor-type units. Four new ovens were constructed, through which the bodies, carried on a continuous conveyor chain, are carried progressively. These are the burn-off, prime coat, first finish coat and second finish coat ovens. The body of each oven is laid on the roof of the building, the work entering and leaving on a vertical ascent from and descent to the top floor. The interior cross section is 10 ft. 10 in. (3.30 m.) high by 6 ft. 4 in. (1.93 m.) wide. The first two ovens are 123 ft. (37.5 m.) long, and the second two 213 ft. (65 m.) long. The bar conveyor itself is 3,220 ft. (982 m.) long and has 251 cross bars spaced 12 ft. 10.5 in. (3.92 m.) apart.

The construction was done in place, and there is no through metal in the oven walls. To make this possible 4 in. (101 mm.) of insulating brick was laid on the building roof and on this the sheet-metal lining was set up, so that it was self-supporting with braces on the inside, and carried the conveyor guides as well. The balance of the insulation was then applied, so that the wall and roof cross section from the inside out shows metal lining, 1 in. (25 mm.) air space, 4 in. (101 mm.) insulating brick and 2 in. (50 mm.) metal lath and plaster.

The electric heater capacity installed was 616 kw. in each of the first two units, and 724 kw. in the third and fourth. Less than one-half of this capacity is needed during the operating

period. To permit control of the heating and cooling curves, ovens No. 1 and 2 are each divided electrically into 5 zones, and No. 3 and 4 into 6 zones, each zone controlled independently and automatically. Part of the heaters in each zone, however, are connected together on a permanent heat circuit which supplies the constant heat losses in the oven.

It was necessary to eliminate dust and dirt from the work while in process, and the space directly underneath the ovens, for the full length of the conveyor, was separated from the rest of the floor by steel and steel sash partitions closely fitted. Air which has been washed, tempered and humidified, is then forced into the room through centrifugal fans, maintaining a small pressure inside this room. This air escapes as oven ventilation and through crevices in the room walls, and an atmosphere is maintained which is practically dust-proof as well as pleasant to work in. A further advantage is had in that there is little or no escape of fumes from the ovens into the enameling rooms. To cut down the dust hazard further, the japanning rooms were floored with hard maple, which is frequently painted with oil, and the oven interiors are systematically wiped down with rags which have been dipped in coal oil.

The progress of the work is as follows: Touring car bodies are received from the inspection department on trucks, pushed under the loading end of the conveyor, and are lifted off by the engagement of a conveyor bar with the hooks on the body hanger straps. As the body passes over the first platform or deck, the interior is sprayed with enamel. The outside is then washed with low-test gasoline applied with rags. This operation removes the scattered spray and softens the grease left on the body by the press dies, and the oil put on the metal for protection against rust. The body then passes up and through the burn-off oven where two objects are accomplished: the enamel is baked on and the grease is burned or charred on the metal and in seams.

The body then passes successively over a sanding deck where uneven spots are lightly sanded, wiped with a tack rag (varnish-dipped cloth) and over the prime coat deck where the enamel is flowed on, over the drip pan and into the prime coat oven. This process is repeated for the first finish coat and second finish coat ovens, and in leaving the latter, the body passes over the inspec-

tion deck where the drippings are removed and it is rigidly inspected under intense light furnished by Cooper-Hewitt lamps, which have been found to be most suitable for this purpose. Defective bodies are sent to the lye-tank room to be cleaned preparatory to re-enameling, and the accepted bodies are loaded on trucks and sent to the assembly line.

With the present cycle of operation, these oven units have a capacity of 36 bodies per hour. The number of bodies in process at any one time is 159.

OVENS FOR FENDERS AND MISCELLANEOUS PARTS.

The enameling of fenders and miscellaneous parts was also done in box-type indirect gas fired ovens. These were replaced by two continuous-conveyor oven units for two-coat work. The oven lengths were 175 ft. (55 m.) and 240 ft. (73 m.), and the electrical capacity installed was 264 and 376 kw. respectively.

Since neither temperature control nor uniformity of temperature were important factors, the metal was still burned off in the gas-fired ovens. As production increased to the point where the capacity of these units was reached, it became necessary to build additional ovens. Three new sets of ovens were constructed, and as it was desirable from the standpoint of durability of finish to do a three-coat job three ovens comprised each set, with installed heater capacity of 486, 480, and 522 kw. respectively. The three sets are side by side and have one common gas-fired burn-off oven. To economize in space the layout is so arranged that the axis of the No. 1 ovens is at 90° with the axis of the burn-off oven, and also at 90° with the No. 2 ovens. A simple monorail conveyor was designed with automatic loading and unloading devices to transfer the work from one bar conveyor to the other.

The old fender ovens are now used to enamel battery boxes, disc wheels, etc.

AXLE OVENS.

On the roof of the die shop ovens were built to enamel the front and rear axles. The front axle receives only one coat, and the oven for this purpose has a capacity of 288 kw. The rear axle housing passes through a first-coat oven, the assembly is completed, including filling the housing with grease, and then through the second-coat oven. The operating temperature of the latter

is only 150° F. (66° C.). The electrical capacity of these two units is 264 and 168 kw. respectively.

CLOSED-BODY OVENS.

The bodies of closed models were formerly made on a wood frame and painted in the customary way. In 1922 a 100 per cent steel body was designed, and the same enameling methods used on the bodies of the open models was made possible. On account of limitations of space in this department, conveyor ovens were out of the question. Twenty-three box ovens were installed, each having a capacity of two bodies.

A truck made of light angle iron carries the body from the start to the finish of the process. The same number of coats is applied as in the open model, and the enamel is flowed on. The burn-off requires only 30 minutes, and the time of bake is one hour. Twelve new ovens were added in 1923. Each of them takes 3 bodies and has 135 kw. in heaters.

ORGANIZATION AND CONTROL.

As constituted at this time there are 984 men working in the enameling plant. Of this number 856 are directly under the superintendent of enameling, and 128 are from the several units in the production department which have some share of the work. The latter are, however, entirely independent, and like the enameling department report directly to the office of the production manager.

Authority to accept or reject finished work is in the hands of the factory inspection department, and it is the standard of quality set by this division which must be met by the enameling department. That this inspection is close is indicated by the number of rejects, which for the box-type ovens is 22 per cent and for the conveyor type 12.5 per cent.

The control of the heating circuits is by electrical department operators. Operating temperatures, however, are specified by the superintendent of enameling. The control of all conveyor ovens is centered in two small buildings, which are located on the roof of the plant. Each heating circuit has a corresponding temperature recording and indicating instrument mounted on a panel, and can be connected so that it is either hand-controlled or automatically operated with instrument control. This is accomplished

by pull switches on the panel, with the operation indicated by colored lights.

The control room operator is in close touch by telephone with the operators at the discharge end of the ovens, so that observed changes in the quality of the work, which are subject to correction by a temperature change, are reported without delay. Should the conveyor speed be changed or a different job started through the ovens he is advised at once.

LOADING OF WORK.

Considerable attention had to be given to the method of loading the work, bearing in mind the limitations set by reflow, ventilation, drip and maximum loading ability. The surfaces of the piece must be so inclined that a free flow of enamel occurs during the dripping period. It is also true that with an enamel of given specific gravity the time of drip must be long enough to allow the excess enamel to flow off.

To obtain proper ventilation, all finished surfaces must be exposed to the current of ventilating air, otherwise the light thinners which are driven off as the work comes up to temperature will become pocketed and wash the metal bare of enamel.

To secure the best loading conditions the hangers or carriers must be made to an exact pattern and the work bunched together closely, due regard being given to the possibility of drip from one piece to another. Improvement of the hanger designs has increased the capacity of the ovens, and at the same time cut down the cost of heat per set of finished work.

VENTILATION.

Experiments are being conducted on the amount of air required per gallon of enamel. While it is claimed that from 2,000 to 2,250 cu. ft. of air is sufficient per gallon (15 to 16.7 cu. m. per liter) in practice this amount is much too low. With too little ventilation the finish has a flaky or "buttermilk" appearance. In laboratory practice 2,200 cu. ft. per gallon (16.4 cu. m. per liter) is sufficient, but in production many times this amount is required It is true, however, that the oven design may be partially responsible for this condition. In the conveyor ovens natural exhaust stacks are installed at both ends of the ovens. These stacks have adjustable dampers that can be locked in various

positions, according to weather conditions and seasons of the year. In the box-type ovens a natural exhaust is used and a certain amount of fresh air is forced in by a fan.

The chemical laboratory has installed meteorological instruments, similar to those used in weather bureaus, to record all atmospheric conditions, and to investigate their relations and influences on enameling and oven ventilation.

HANDLING AND CARE OF ENAMEL.

Enamel is bought from the manufacturer to conform as to the percentage and kind of oil, gum, thinners and pigment, with the analysis which has been found most suitable for the work. This analysis is checked by the chemical laboratory, and at the same time physical tests are made for the purpose of checking the color, viscosity, baking time and temperature, fineness of pigment, toughness of coat, and luster. All material is inspected at the manufacturers' plant, and the drums are also inspected for cleanliness before filling.

Approximately 1,500 drums of 54 gallons (205 liters) capacity each are carried in stock. When this enamel is needed, it is pumped out of the drums into a make-up tank, thinned out to the proper viscosity, and pumped into the feed lines to the dip tanks or flow guns.

From the dip tanks of the ovens that bake the fender and miscellaneous parts this enamel can be circulated in much the same way. The customary practice, however, is to withdraw the enamel once or twice a week to be clarified or filtered. In this way the small amount of dirt which comes through on the work and is washed off by the enamel is removed. The dust or dirt particles that stick to the metal in passing through the dip are baked on, and must be removed at the sanding deck; otherwise, their size will be exaggerated with each succeeding enamel coat.

To secure uniformity of flow of the enamel it is necessary to maintain a constant temperature in the enamel tanks as well as in the rooms. Should the enamel temperature be too high, cold water is circulated through pipe coils, which are submerged in the dip tanks. When the temperature becomes too low it is brought back to normal by electric heaters which are arranged around the outside of the tanks.

Should one of the dip tanks catch fire the breaking of a fusible link opens a 6-in. quick-opening valve, and drops the enamel into one of several 7,000-gal. (26,000 liter) fire tanks.

COST OF HEAT.

Due to the fact that there is such a diversity of work passing through the different conveyor ovens, it is almost impossible to segregate costs for any one part. The average cost per car, however, is an exact figure. This has been determined for the first 6 months of 1924, and is the cost of 484 kw.-hr. of current.

CONCLUSION.

There have been changes made in the design of conveyor enameling ovens with the object of conserving heat, and reports indicate their successful operation. This applies to all types, those using electrical energy and others. The use of cellulose base materials, which require little or no heat, is also making rapid progress, as it did in the furniture industry.

DISCUSSION.

T. B. Hine[3]: Has any difficulty been encountered in electric japanning ovens, due to explosions from the solvent vapors mixed with air in contact with the hot resistor wires? I heard rumors that some of the electrically-heated japanning ovens have exploded, and caused casualties at times.

C. F. Hirshfeld[4]: In order to have an explosion you must have two things: A mixture of such proportions that it can burn rapidly and a source of ignition. You may get your source of ignition from the heaters or resistors themselves, if they are operated at a sufficiently high temperature, or from a carbonaceous deposit which has resulted from the gradual change in drops of japan on some part of the oven. These drops form a spongy material, which ultimately ignites spontaneously. In the modern oven we do three things: We carefully control the mixture, so that it does not attain explosive proportions; we keep the oven fairly clean of deposits of japan, so that we do not have an opportunity to build

[3] Research Chemist, Western Electric Co., Chicago, Ill.
[4] Chief of Res. Dept., The Detroit Edison Co., Detroit, Mich.

up a spongy carbonaceous material, and we operate heaters at a comparatively low temperature.

WIRT S. SCOTT[5]: We have gone into the question of the hazard due to possible explosions in ovens very thoroughly, and it is our opinion that the explosion is due to improper ventilation in the oven rather than to the high temperature of the heaters. Looking at the situation from a practical standpoint, there is always a possibility of having an electric arc occur in an oven. In other words, no one can guarantee that an arc will not form by a connector coming loose, or some break in the circuit of that sort. Accordingly, even if you attempt to put in heating elements which normally will operate at a very low temperature, there is always this possibility of having an arc occur in the oven. Therefore, sufficient ventilation must be supplied to prevent an explosion even under these conditions.

In our plant at East Pittsburgh we had an explosion in an impregnating tank in which we used a certain type of varnish, heating by steam at 250° F. (121° C.). We had a severe explosion, and on the basis of other tests we have made on enamels we are convinced that it is a matter of ventilation more than anything else. From tests we have made, using 95 per cent air to 5 per cent solvent, by weight, gives you a non-explosive mixture. However, if you use 85 per cent air to 15 per cent solvent by weight, you get the most violent explosion that can be obtained. With 70 per cent air and 30 per cent solvent, you will get a less violent explosion, because you have a carbon-rich mixture. With this last proportion there is always the possibility, particularly when you are using the box type oven, that if the door should open the inrush of air would cause an explosion. That has happened several times to my knowledge. From our standpoint we are convinced it is a question of using the proper amount of ventilation. We know from past experience that gas ovens have operated, many of them, for years without exploding.

W. W. MURRAY[6]: Has there ever been any case of an explosion with ovens of the continuous type, open at both ends, assuming, of course, that the ovens have ventilating equipment that removes vapors as rapidly as they rise from the japan or enamel?

[5] Westinghouse Elec. and Mfg. Co., East Pittsburgh, Pa.
[6] Chemist, Continental Can Co., Inc., Chicago, Ill.

WIRT S. SCOTT: I do not know of any case where an explosion has occurred in a continuous type of oven. I do not see how it would be possible. As a matter of fact, our chairman, Mr. Hirshfeld, made some experiments several years ago along that line, and as I recall the results were these: An oven would have to be of such a length that the length would equal 200 times the diameter before you could get a perceptible explosion. Is that correct?

C. F. HIRSHFELD: Yes, something of that nature. At any rate, we got an answer which looked right, and I marked it off the books.

L. A. DANSE[7]: Have any of the gentlemen present conducted experiments in enameling by heating the air and then passing that through the oven to heat the work.

E. F. COLLINS[8]: This was first done a number of years ago. I have definite results on ovens heated by passing hot air over charges. I can not quote them as I haven't them in mind, but such work has been done.

WIRT S. SCOTT: We have made some tests along that line, not for enameling, but for core baking, where a large amount of air was required. In every case the efficiency was much lower in using the air method of heating. As far as enameling is concerned, I don't see what could be gained by heating with air. As a matter of fact, I think the air would be more or less of a detriment to the proper heating of enamels.

E. F. COLLINS: I want to give one or two particular cases which show how it has been used to advantage: The enameling of shoe eyelets, drying effervescent chemicals, drying foundry cores, drying bristle brushes, etc.

HARRY ALLEN: We had one small explosion in an enameling oven, and I think it bears out the point that it was lack of ventilation. Temporarily we were using a box oven for burning off bodies. The operator made a mistake and pushed a wet body into the oven and it exploded. That is the only explosion we have had.

[7] Metallurgist, Cadillac Motor Car Co., Detroit, Mich.
[8] Consulting Engr., General Electric Co., Schenectady, N. Y.

A paper presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 3, 1924, Mr. F. A. J. FitzGerald in the Chair.

PHYSICAL CHARACTERISTICS OF SPECIALIZED REFRACTORIES.

Part V—Thermal Conductivity of Carborundum Refractories.[1]

By M. L. Hartmann[2] and O. B. Westmont.[3]

Abstract.

Thermal conductivity measurements up to 1,350° C. of silicon carbide refractory materials have been made, using the water calorimeter method. Data were secured on furnace walls, such as those commonly used in practice, and results are believed to be accurate to within about one per cent. Conductivity measurements were made on seven carborundum single walls and on eight carborundum-fireclay composite walls. The relation of the thermal conductivity to temperature, chemical composition, and porosity was investigated, as well as the magnitude of the surface and joint effects. The conductivity of carborundum refractories was found to vary with the quantity of heat energy transmitted through the wall. Tables are given showing the coefficients of thermal conductivity and heat flow through various types of walls, with a temperature of 1,500° C. in the combustion chamber.

Of all the refractory materials available commercially, there is none which even approaches silicon carbide or carborundum in its ability to transmit heat readily, and at the same time possess sufficient mechanical strength and chemical inertness to resist the various destructive forces in modern industrial furnaces. The great mechanical strength of commercial refractories made from carborundum has been previously studied,[4] but accurate informa-

[1] Manuscript received July 15, 1924.

[2] Director of Research Laboratory, The Carborundum Co., Niagara Falls, N. Y.

[3] Research Chemist, The Carborundum Co., Niagara Falls, N. Y.

[4] Hartmann and Hougen, Trans. Amer. Electrochem. Soc., 37, 707 (1920); Hartmann and Kobler, Trans. Amer. Electrochem. Soc., 37, 717 (1920); Hartmann and Koehler, Trans. Amer. Electrochem. Soc., 40, 457 (1921).

tion concerning their ability to transfer heat under actual operating conditions has been lacking.

A number of investigators have studied the thermal conductivity of refractory materials, but insofar as silicon carbide refractories are concerned, the results are not concordant, nor has the investigated range of temperatures been sufficiently high. The variation in the published results is perhaps due not only to the difference in the methods used, but also to the differences in the burning temperature, porosity and chemical composition of the refractories tested.

The thermal conductivity of silicon carbide refractories at low temperatures recorded by Wologdine[5] agrees with the data published several times by The Carborundum Company.[6] These data, however, are quite different from those published recently by Beecher.[7] The results of Watts and King[8] are relative, and can not be compared directly with the values of other investigators. The curve published by M. L. Hartmann[9] represents values secured during the preliminary experimental work recorded herein.

The remarkable increase in the use of carborundum refractories, in furnaces requiring a transfer of thermal energy through partition walls, makes it desirable to determine accurately not only the relation of the thermal conductivity to temperature, but also its relation to the composition and to the porosity of the refractories.

In many installations, the carborundum refractories are insulated so as to prevent rapid heat flow, with the result that the temperature gradient is relatively small. In calculating heat balances in such furnaces, it has been assumed in accordance with Fourier's law that the thermal conductivity of the refractory is independent of the temperature gradient, and that the heat flow through the composite walls is inversely proportional to the thermal resistivity of each wall.

There appears to have been little experimental work published to determine if the thermal conductivity at a given temperature

[5] Wologdine, Electrochem. and Met. Ind., 7, 383 (1909).

[6] Linbarger, Chem. and Met. Eng., 19, 489 (1918); Circular, The Carborundum Co. (1921).

[7] Beecher, Jour. Amer. Cer. Soc., 7, 19 (1924).

[8] Watts and King, Jour. Amer. Cer. Soc., 6, 1075 (1923).

[9] Hartmann, Refractories for Electric Furnaces, Booklet, The American Electrochem. Soc., p. 69 (1924).

is a constant, regardless of the quantity of energy being transferred. According to the Bureau of Mines Report,[10] the question of the variation of thermal conductivity with different temperature gradients has been raised by Professor E. B. Wilson, recently of the department of physics of Massachusetts Institute of Technology. Fourier's law[11]

$$Q = k \frac{A\ (t_1 - t_2)}{L}$$

assumes that the conductivity, k, while of course different at different temperatures, is strictly a constant for all values of the temperature gradient $\frac{(t_1 - t_2)}{L}$. Prof. Wilson has pointed out that there is a possibility that this law of heat conduction may not be exactly realized when large temperature gradients are involved.

In single carborundum walls the transferred heat energy is much greater than in the more usual refractory materials, and hence it seemed desirable to determine whether or not Fourier's law does hold under these unusual conditions. To do this it was necessary to test several composite walls, in which the heat flow was decreased by insulation.

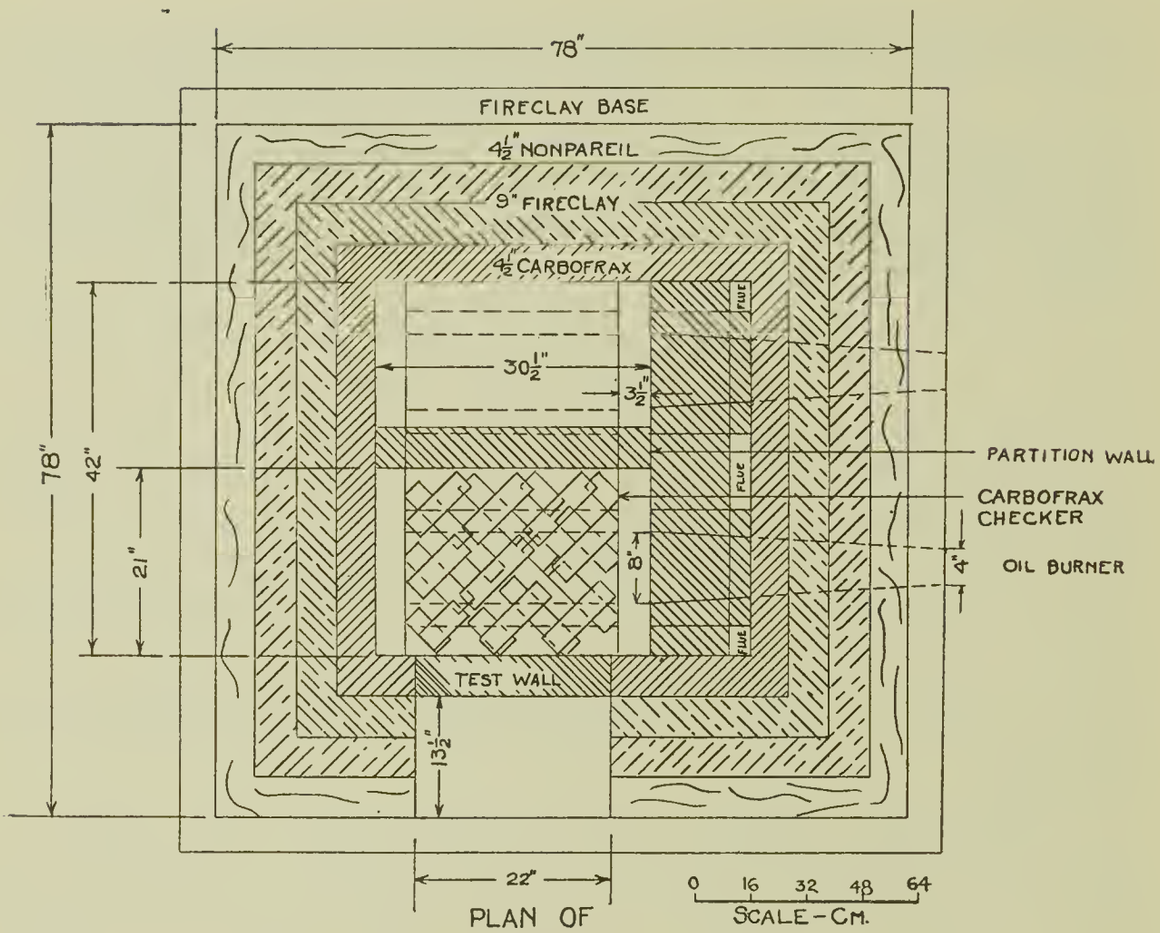
The most practicable method of measuring the thermal conductivity of refractories, under conditions approaching those in practice, is the method used by Boyd Dudley.[12] This method does not require the use of special shapes, which may have different thermal properties from those of the commercial bricks. The wall under test is built of standard 6 x 11 x 23 cm. (2.5 x 4.5 x 9 in.) bricks laid up with cement of the same composition as the bricks. The heat transmitted through a definite area of this wall is measured by a waterflow calorimeter 20 cm. (8 in.) square fitted with a 5 cm. (2 in.) guard ring. This guard ring prevents lateral flow of heat. The temperature gradient through the wall is measured by thermocouples inserted to various depths in holes bored to within 6 mm. (0.25 in.) of the inner face.

For the determination of the thermal conductivity up to 1,400°

[10] Hersey and Butzler, Report of Investigations, Serial No. 2564, Jan., 1924.

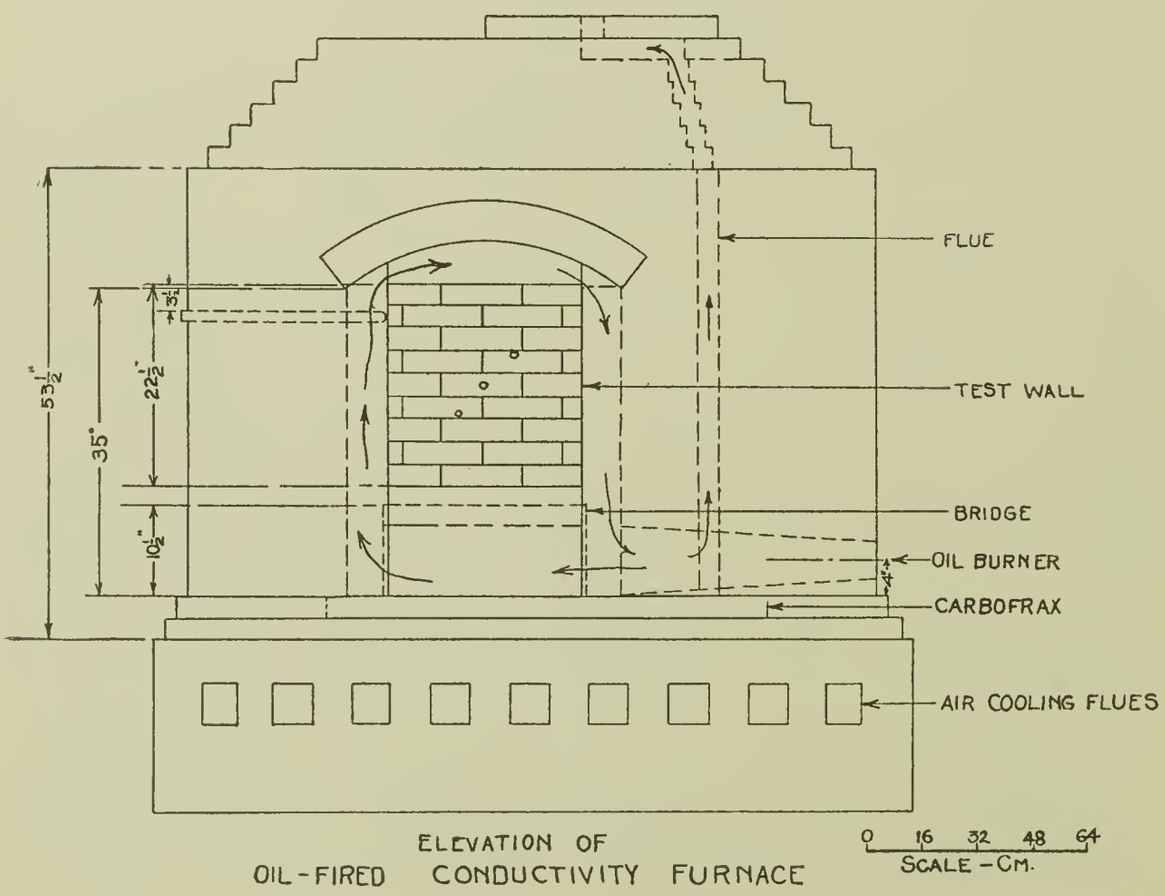
[11] Throughout this paper Q = heat flow, k = thermal conductivity, A = area, L = thickness, $t_1 - t_2$ = temperature drop.

[12] Dudley, Trans. Am. Electrochem. Soc., 27, 285 (1915).



PLAN OF OIL-FIRED CONDUCTIVITY FURNACE

FIG. 1



ELEVATION OF OIL-FIRED CONDUCTIVITY FURNACE

FIG. 2.

C., it was found that the 5 cm. guard ring used by Dudley did not insure normal flow of heat through that section of the wall under test. (The highest temperatures obtained by Dudley were not over 1,000° C.) For this reason, an additional guard ring was used in our apparatus for the high-temperature tests.

APPARATUS.

The furnace used for the conductivity tests is shown in Fig. 1 and 2. This furnace was larger than required, so a partition wall was built in the center and only the portion near the test wall was used. One large oil burner, operated with 3 kg. (6.6 lb.) air pressure, was used to heat this portion of the furnace. A checkerwork was made with carborundum bricks, as shown, so that the oil flame passed below a bridge supporting the checker and around the checker to flues. It required approximately 12 hr. to heat this furnace to 1,500° C. The pressure in this furnace at 1,500° C. was found to be + 1.3 mm. (0.05 in.) water.

The calorimeter (Fig. 4) used was designed after the one described by Dudley. The second guard ring (Fig. 5) was made similar to the first guard ring, which provided for double circulation of water. This guard ring was connected directly to the main water line, while the calorimeter and first guard ring were connected to a 60-gal. supply tank, in which a constant pressure was maintained. The face of the calorimeter away from the furnace was covered with a 3 mm. (0.125 in.) asbestos board, in order to reduce the heat transfer to or from the surrounding air. The thermal conductivity of this cover plate was determined accurately for various temperature differences, by the method described by Dudley. The temperatures were measured simultaneously at the three points in the wall under the calorimeter by means of three Pt: Pt-Rd thermocouples, attached to a slider and supported on the framework (Fig. 3). Three holes 13 mm. (0.5 in.) in diameter, drilled to 6 mm. (0.25 in.) from the hot surface, were fitted with sillimanite pyrometer protection tubes, in which the three thermocouples were inserted to any measured position.

Measurements of temperature gradients in this manner are subject to certain small errors. The protection tubes are of different material from the brick wall; the thermocouple junction is

exposed to radiations from the hot end of the hole; convection currents around the tube and the couple may alter the readings.

To determine the magnitude of these possible errors we repeated the tests which Dudley described, going to temperatures as high as 1,450° C. Temperature measurements were made in a fireclay wall (1) in open holes, (2) open holes with a protection tube liner, (3) in a hole closed with clay pieces. The temperature readings in the three cases were identical within the limits of experimental error.

The differential couples were made of 30 B. & S. gauge (0.25 mm.) copper and constantan wire, which was tested and found to be practically homogeneous. The couples were made by mounting the wires on a cardboard, and then fusing the ends together in an electric arc. Two separate couples were made up in this manner, one composed of 24 junctions for use in measuring the rise in temperature of the calorimeter water, and the other composed of 12 junctions for use in measuring the difference in temperature of the outlet water from the calorimeter and inner guard ring.

The junctions of the couples were wrapped separately with thread, and dipped in cellulose acetate solution, to prevent short circuiting. The legs of each couple were then sealed in 6 mm. glass tubes with the same solution. The junction to the lead wires of both of these couples were sealed with casein in test tubes, which were immersed in oil in order to insure equal temperatures. These couples were calibrated with standard thermometers, so that temperature differences up to 40° C. could be read directly to 0.05° C. The differential couple temperatures were measured by the use of a precision potentiometer.[13]

Method of Conducting Tests.

Before making up the test walls the bricks were arranged in the position in which they were later to be placed in the wall. It was necessary to grind down the faces of several of the bricks so that they would fit together closely. The bricks were then placed approximately 0.8 mm. (1/32 in.) apart to allow for the layer of cement, and, by the use of a templet the position of the three holes for measuring the temperature gradient was marked.

[13] This electrical measuring equipment was designed and installed by W. G. Soley, of this laboratory, whose valuable assistance is hereby acknowledged.

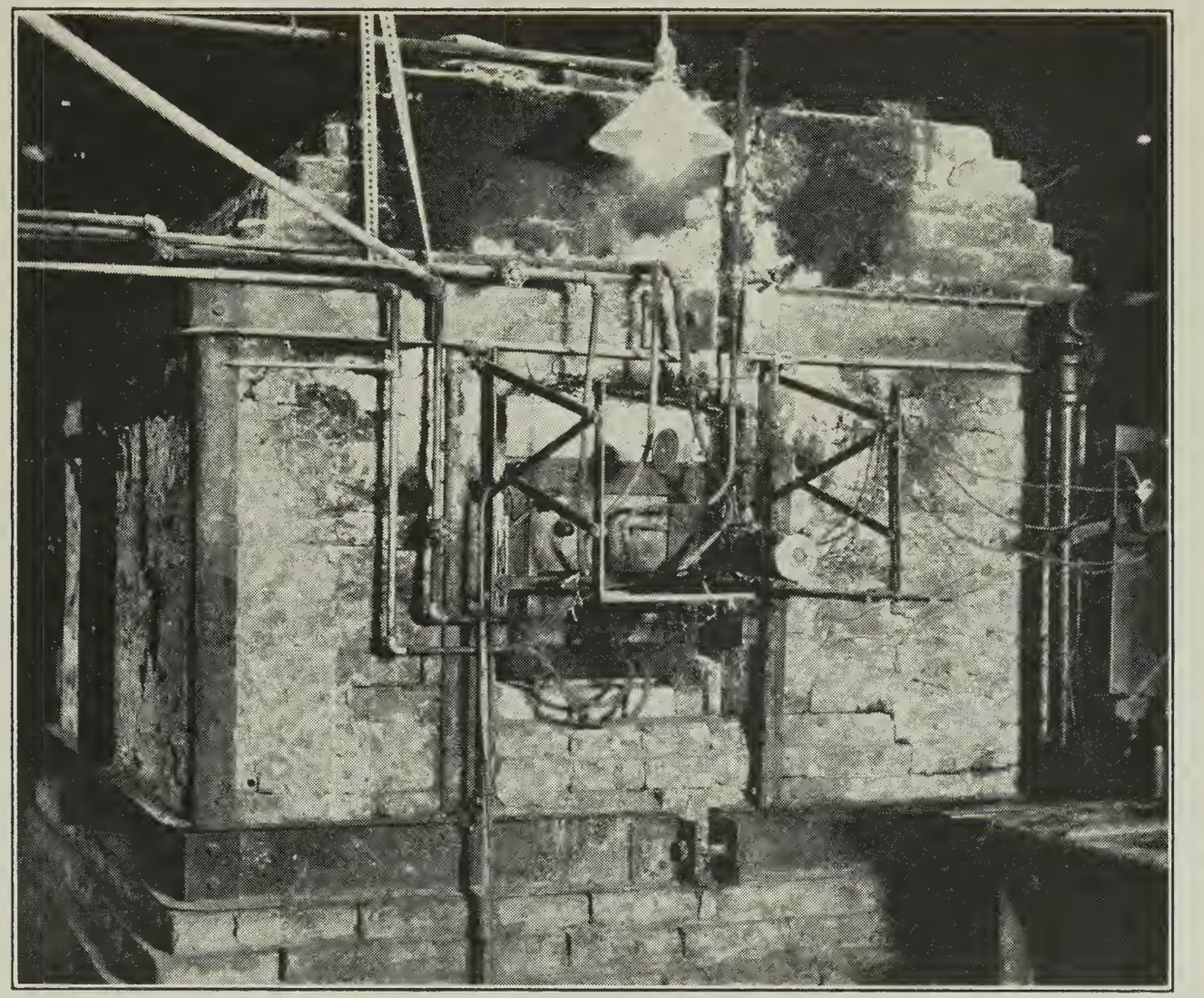


Fig. 3. Furnace for testing heat conductivity of refractories.

The thermal conductivity tests were made on the following walls:

1.....23 cm. carborundum, No. 1A
2.....11 cm. carborundum, No. 1B
3.....11 cm. carborundum, No. 1C
4.....11 cm. carborundum, No. 2
5.....11 cm. carborundum, No. 3
6.....11 cm. carborundum, No. 4
7.....11 cm. carborundum, No. 5
8.....23 cm. carborundum, No. 1A and 11 cm. fireclay, No. 26
9.....23 cm. carborundum, No. 1A and 11 cm. fireclay, No. 75
10.....11 cm. carborundum, No. 1C and 11 cm. fireclay, No. 26
11.....11 cm. carborundum, No. 2 and 11 cm. fireclay, No. 26
12.....11 cm. carborundum, No. 2 and 11 cm. fireclay, No. 75
13.....11 cm. carborundum, No. 3 and 11 cm. fireclay, No. 26
14.....11 cm. carborundum, No. 4 and 11 cm. fireclay, No. 26
15.....11 cm. carborundum, No. 5 and 11 cm. fireclay, No. 26

The bricks used were all standard 6 x 11 x 23 cm. (2.5 x 4.5 x 9 in.).

In the 23 cm. walls the bricks were placed so that the temperature gradient was through the 23 cm. dimension. In the 11 cm. walls they were placed so that the gradient was through the 11 cm. dimension.

In the tests on composite walls the carborundum walls were insulated with fireclay bricks. These bricks were arranged so that the gradient was through the 11 cm. dimension. The temperature gradient holes through the insulating walls were made to coincide with those in the carborundum wall. The joints of the two walls were made to mis-match as much as possible.

The carborundum test bricks were all laid up with a fine plastic carborundum cement, of similar composition to that of the bricks. A plastic fireclay cement was used in laying up the fireclay bricks. After the wall was completed the surface under the calorimeter and guard rings was covered with a thin layer of the same cement, which was later smoothed off and made perfectly flat with a steel straight-edge.

After completing the conductivity test on the single wall, the insulating wall was laid up in the same manner. A thin layer of fireclay was also placed between the walls to insure perfect contact.

After drying the test wall, the calorimeter and guard rings were placed against it, so that the temperature gradient holes in the bricks coincided with those in the calorimeter. The apparatus was then held firmly against the wall, by means of clamp screws that were fitted to the framework shown in Fig. 3.

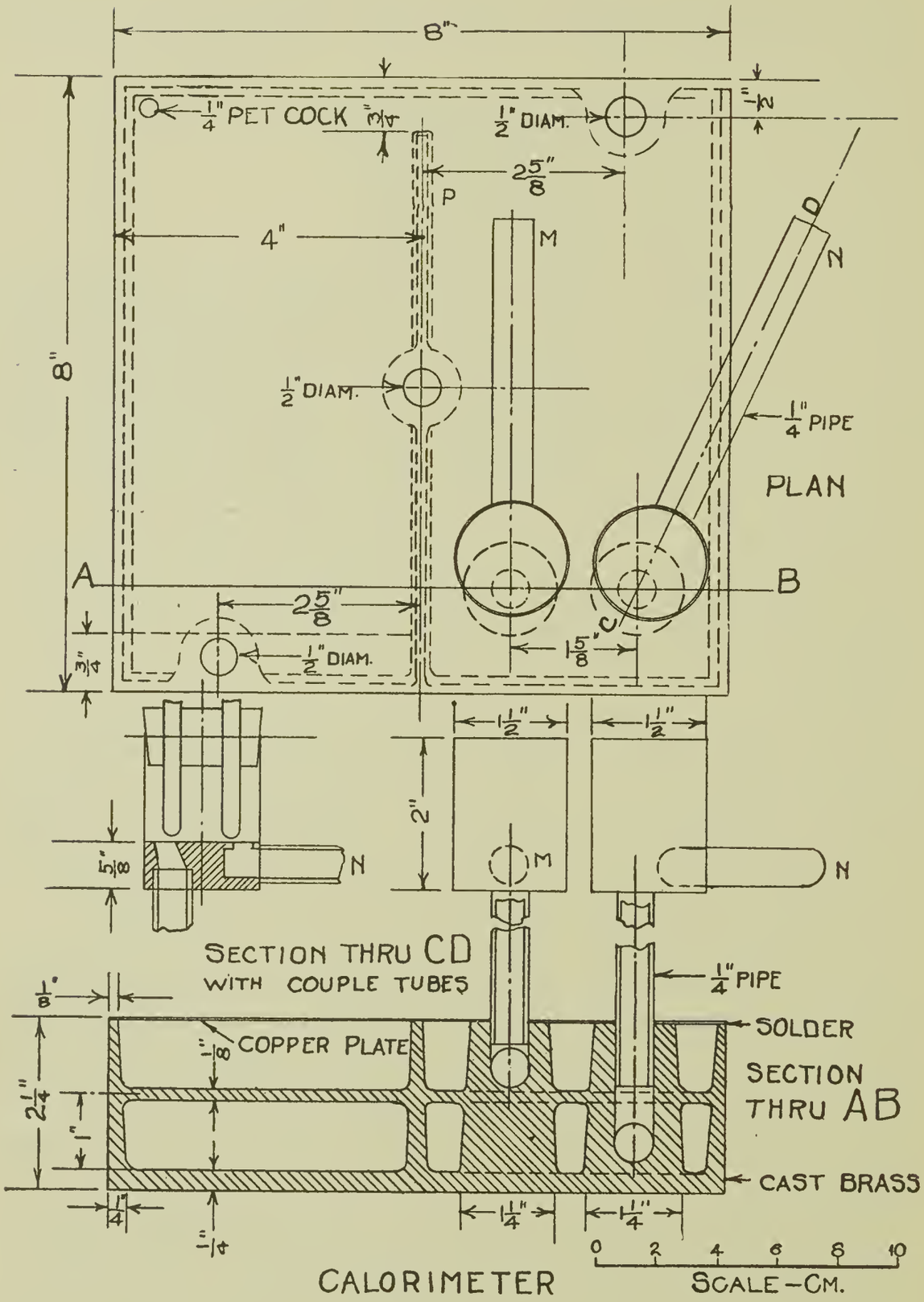


Fig. 4.

After the calorimeter (Fig. 4) and guard rings (Fig. 5) were adjusted, the apparatus was connected to the water lines. The furnace was heated for approximately 12 hours to obtain 1,500° C. in the combustion chamber. The oil supply to the burner was then

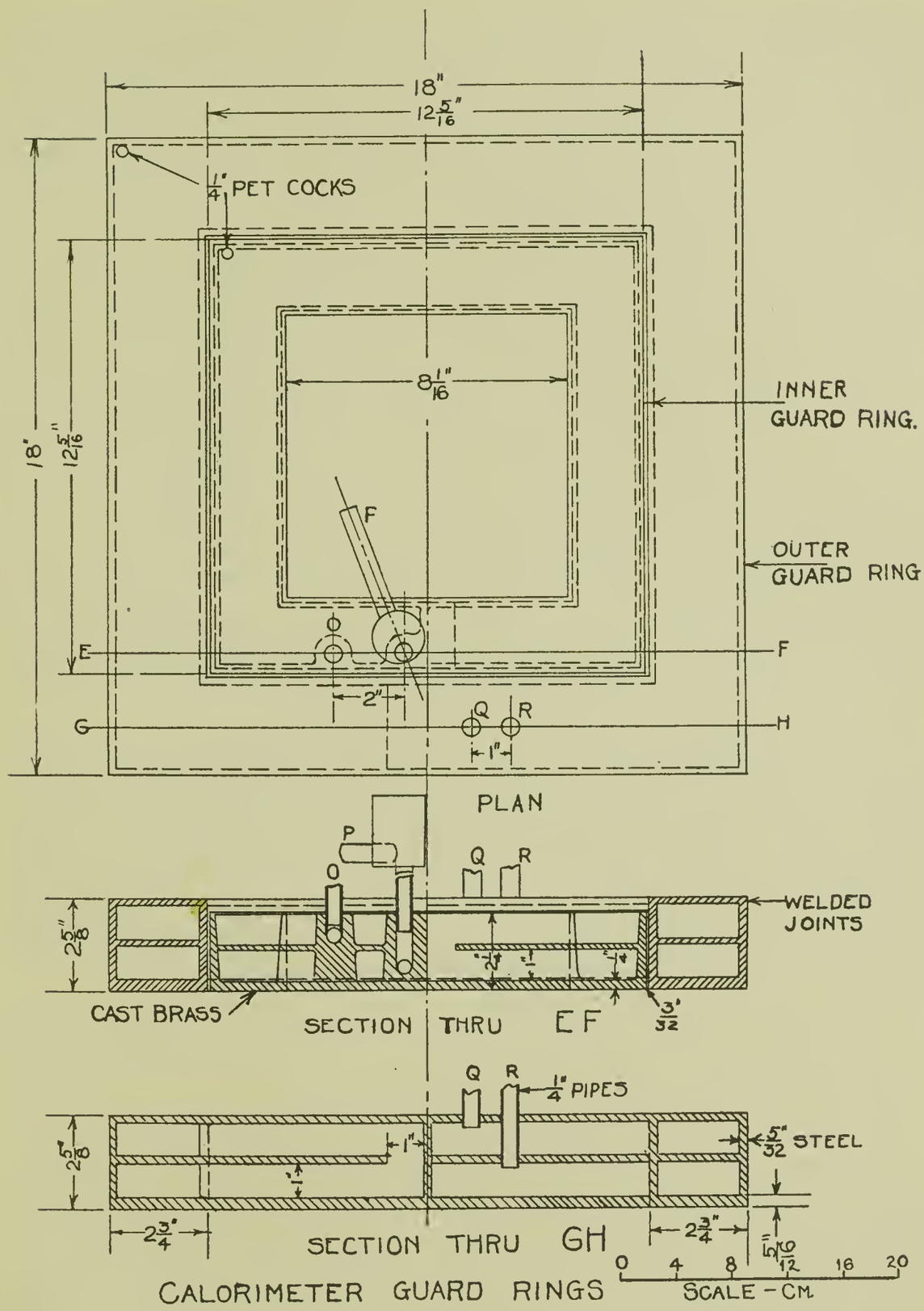


FIG. 5.

regulated so that the temperature of 1,500° C. ± 15° C. would be maintained throughout the test. The air supply to the burner was kept constant. In the meantime, the clamp on the outlet tube from the calorimeter was regulated so that the flow of water was not

more than 3 kg./min. The clamp of the outlet tube of the inner guard ring was also regulated, so that the temperatures of the water from the calorimeter and guard ring were approximately the same. The flow of water through the outer guard was hand regulated throughout the test, so that the temperature was within 5°C. of that of the calorimeter.

After the furnace had been kept at equilibrium for approximately 30 min., the rise in temperature of the calorimeter water was determined by the potentiometer, and the difference in temperature of the calorimeter and guard ring outlet water also determined. Close adjustments were then made on the outlet tube of the inner guard ring, until the temperature difference in the outlet water of the two compartments was within 0.2° C., that is, 10 cm. deflection as indicated by the galvanometer. If the change in potentiometer reading was not over 1 cm. or 0.1° C. in 30 min., the furnace and apparatus was considered to be in equilibrium, and ready for the test. It usually required 2 to 2.5 hr. to secure equilibrium after the furnace was heated to 1,500° C.

The three thermocouples for measuring the temperature gradient were fitted with 3 mm. 2-hole insulators, and inserted in the protection tubes and pushed back as far as possible into the holes in the wall. The insulators were then clamped to the slider, and the elements were bent so as to prevent any movement through the insulators. The cold junctions of the couples were inserted into glass tubes in a thermos bottle filled with ice.

With the couples arranged in this manner, they were connected to a potentiometer, and the temperature readings taken simultaneously in three points in the wall.

After the apparatus was in equilibrium and the couples arranged as described above, the actual test was started. The first temperature gradient readings were taken with the couples in the wall at full depth. The slider was then pulled out 1 cm. (0.4 in.) and readings taken. This was repeated until the slider reading was 10 cm. (4 in.), after which the couple was moved to its original position and the readings taken. During this time the water passing through the calorimeter was collected and weighed. After balancing the dry cells of the potentiometer against the standard cell, the slide-wire readings were taken for zero deflection of the galvanometer. The temperature difference between

the outlet water of the calorimeter and inner guard ring was also read. If the deflection was greater than 10 cm. or 0.2° C. adjustments were made on the clamp on the outlet tube of the guard ring, to equalize the temperatures. Temperature readings were taken every 5 min. for 1 hr. The total weight of water flowing through the calorimeter during that time was then obtained.

With the thermocouples in their original position the same process was repeated as a check test. Thus for 11 cm. walls two 1-hr. tests were made with the furnace at practically a constant temperature. For the composite walls each test required 1.5 hr. The temperature gradient readings were taken every 13 mm. instead of every 10 mm. as in the 11-cm. walls.

After completing the tests on a wall, the couples were marked at the end of the protection tubes when they were at full depth. The protection tube was also marked at the face of the calorimeter. The couples and tubes were then removed and measurements taken to determine accurately the depth of the hot junction of each couple in the wall at the initial position.

CALCULATION OF THERMAL CONDUCTIVITY.

With the temperature of the inner guard ring equal to that of the calorimeter, the total heat flow Q_T from both faces of the calorimeter was equal to the sum of the heat flow from the test wall Q_W and that from the air, Q_A, through the opposite face. The value of Q_T was found by the formula:

$$Q_T = \frac{W \times t}{T \times A}$$

where

W = wt. of water in g.
t = ° C. rise in temp. of water
T = time in seconds
A = area of the calorimeter in sq. cm.

Therefore, Q_T is in gm. calories/sq. cm./sec. Q_A was determined by the formula:

$$Q_A = K_1(t_1 - t_2)$$

where

K_1 = Ther. cond. of 3 mm. asbestos cover in gm. cal./sq.cm./°C./sec.
t_1 = Temp. in °C. of air 2.5 cm. (1 in.) in front of calorimeter.
t_2 = Av. Temp. °C. of calorimeter = $t_3 - t/2$, where t_3 is the temp. of the outlet water of the calorimeter.

Therefore $Q_T - Q_A = Q_W$ in gm. cal./sq. cm./sec.

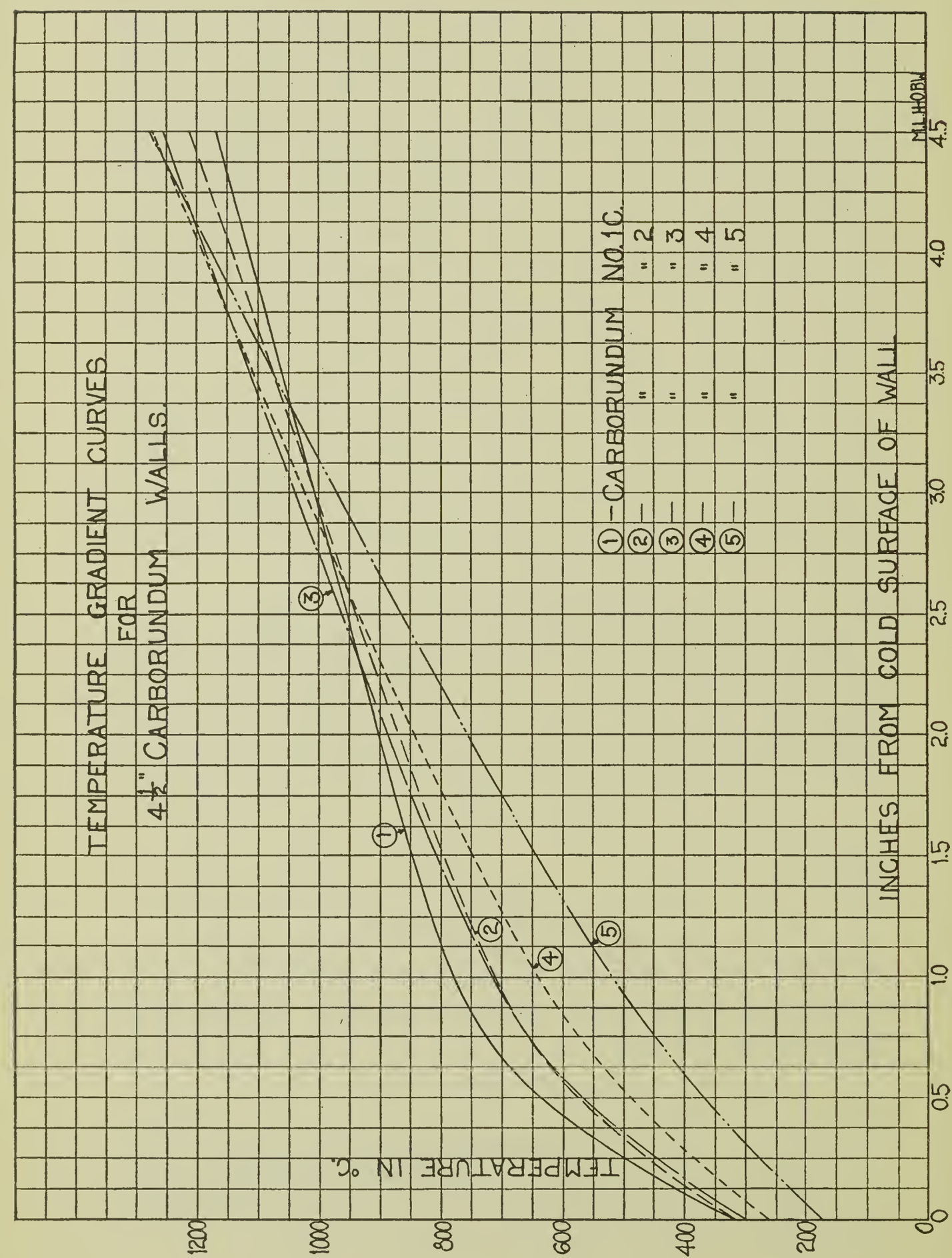

TEMPERATURE GRADIENT CURVES
FOR
4½" CARBORUNDUM WALLS.
① - CARBORUNDUM NO. 1C.
② — " 2
③ — " 3
④ — " 4
⑤ — " 5
INCHES FROM COLD SURFACE OF WALL
TEMPERATURE IN °C.
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
200
400
600
800
1000
1200
M.L.H.O.B.W.

Fig. 6.

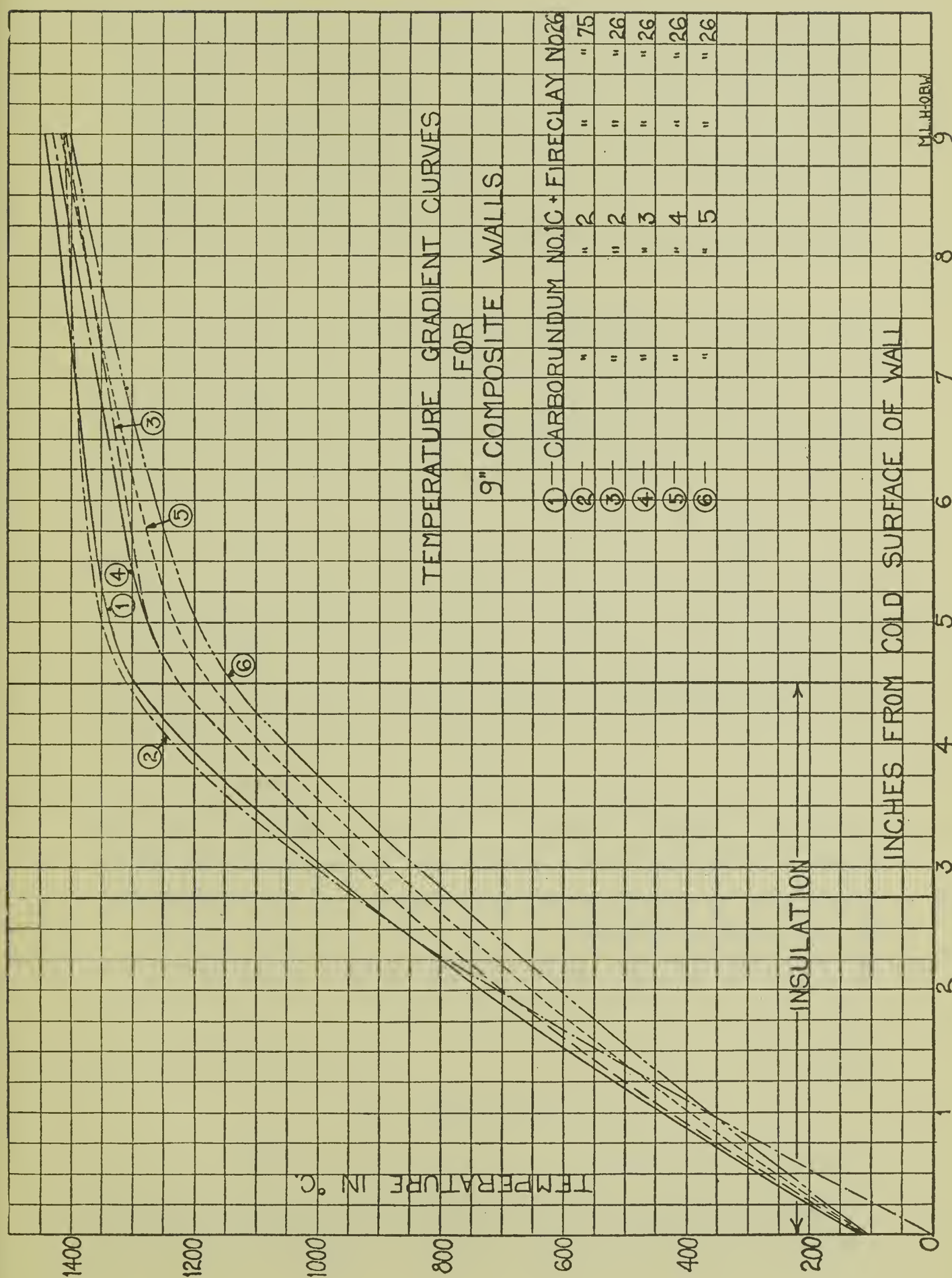

TEMPERATURE GRADIENT CURVES
FOR
9" COMPOSITE WALLS
① — CARBORUNDUM NO.1C + FIRECLAY No26
② — " 2 " " 75
③ — " 2 " " 26
④ — " 3 " " 26
⑤ — " 4 " " 26
⑥ — " 5 " " 26
INSULATION
INCHES FROM COLD SURFACE OF WALL
TEMPERATURE IN °C.
0
200
400
600
800
1000
1200
1400
1
2
3
4
5
6
7
8
9
M.L.H.&R.W.

Fig. 7.

Since the temperature gradients and the heat flow for the two tests did not vary over 2-3 per cent, the averages were taken for the determination of the thermal conductivity. With greater variations the tests were repeated. The average temperature gradient curves for the single and composite walls are shown in Fig. 6, 7 and 8. These curves are extrapolated through the last 6 mm. (¼ in.) to the fire side of the wall. They were originally plotted so that temperatures could be read directly to 2° C. and

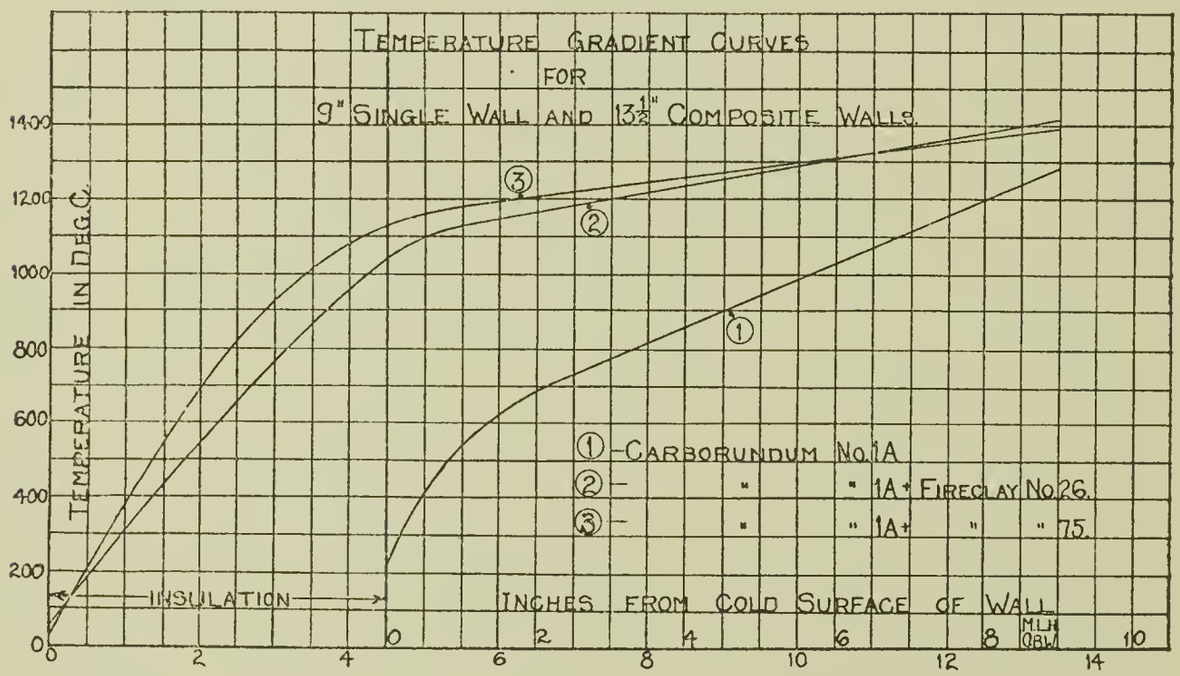


FIG. 8.

distances to 0.25 mm. (0.01 in.). By the use of these curves the gradient or temperature drop per unit distance could be determined very accurately at any temperature and the conductivity, K, calculated as follows:

$$K = \frac{Q_w \times L \times 2.54}{(t_1 - t_2)}$$

where

L = distance in wall in inches
$t_1 - t_2$ = temp. drop in °C.

Therefore, K is in gm. cal./cu. cm./°C./sec.

This graphical method of determining the temperature gradient was found to be less involved and more accurate than the one

used by Dudley. He assumed that the temperature gradient curve was a section of a parabola, and calculated the equation of the curve from three known points. The thermal conductivity at different temperatures was then determined by taking the first derivative of the equation. Obviously starting with the assumption that the temperature gradient curve was a parabolic section, the thermal conductivity-temperature curves were necessarily straight lines, since the first derivative of a second-degree equation is a linear function.

In our work it was found that the thermal conductivity-temperature curves were not all linear functions. It was also found that it was practically impossible to calculate an equation for the gradient curve that would fit the actual data accurately. For these reasons the above described graphical method was used for calculating thermal conductivities.

BRICKS USED FOR THERMAL CONDUCTIVITY TEST.

The No. 1A, 1B, 1C bricks were made of carborundum recrystallized in an electric furnace. The other carborundum bricks contained ceramic bonds, and were kiln burned at approximately 1,350° C. The bricks No. 26 were coarse, fairly open, first quality fireclay. Bricks No. 75 were extremely porous fireclay products, also burned at about 1,350° C.

In selecting the bricks for test the apparent densities of several were first determined, and only those whose apparent densities were near the average of the lot were used in the test wall. In the wall directly under the calorimeter the bricks with no greater variation in apparent density than 0.04 grams per cc. were used.

After the completion of the tests on each wall the bricks under the calorimeter were sampled for chemical analysis. The samples were taken from the central, vertical section of the test wall. The average apparent density and chemical analyses of the bricks are recorded in Table I.

RESULTS.

In the preliminary work a 23 cm. carborundum wall was used, and checks made on two separate runs (No. 3 and 5). Tests were then made on the same wall backed with various kinds of insulation, after which another run (No. 10) was made on the 23 cm.

TABLE I.

Apparent Density and Chemical Analyses of Bricks.

	Carbo No. 1A	Carbo No. 1B	Carbo No. 1C	Carbo No. 2	Carbo No. 3	Carbo No. 4	Carbo No. 5	Fireclay No. 26	Fireclay No. 75
Apparent density g. per cc.	2.05	2.07	2.20	2.48	2.35	2.36	2.31	2.05	0.67
*Porosity..	34.10	33.80	29.50	18.40	20.70	17.70	18.90	26.80	74.20
Ignition...	0.17	0.00	0.00	0.88	0.24	0.02	0.10	0.31	0.00
SiO_2....	8.02	4.50	4.50	14.72	23.31	36.80	38.76	58.50	56.90
SiC.....	91.51	93.20	93.20	80.10	68.50	52.60	48.35	.....	.....
Al_2O_3...	0.20	1.33	1.33	1.47	5.58	8.10	11.63	34.48	37.70
Fe_2O_3...	0.65	1.03	1.03	1.33	1.57	1.97	1.97	3.52	2.37
TiO_2....	....	....	....	....	....	....	....	1.80	1.74
CaO....	....	....	....	....	....	....	....	0.29	0.82
MgO....	....	....	....	....	....	....	....	0.62	0.20
Total ...	100.55	100.06	100.06	98.50	99.20	99.49	100.81	99.52	99.73

* Calculated, assuming Sp. Gr. SiC = 3.17; Sp. Gr. Fireclay = 2.60.

wall to check the original results, and to determine if there was any change in the conductivity due to changes in the refractories. The results of the three runs on the 23 cm. wall are given in Table II. These tests show that the results on a given wall can be relied upon to within approximately 1 per cent.

TABLE II.

Thermal Conductivity of Carborundum Walls.

Run No.	Temperature ° C.	Heat Flow Gm. cal./ sq. cm./sec.	Ther. Conductivity Gm. cal./cu. cm./° C./sec.	
3a	640-1295	1.525	0.0416	
3b	665-1340	1.582	0.0417	
5a	685-1320	1.392	0.0390	
5b	678-1330	1.498	0.0408	
Average...	.....	1.499	0.0408	±0.0004
10a	672-1205	1.305	0.0404	
10b	710-1283	1.358	0.0391	
Average...	.....	1.331	0.0398	±0.0005
Average of three runs	.....	1.415	0.0403	±0.0004

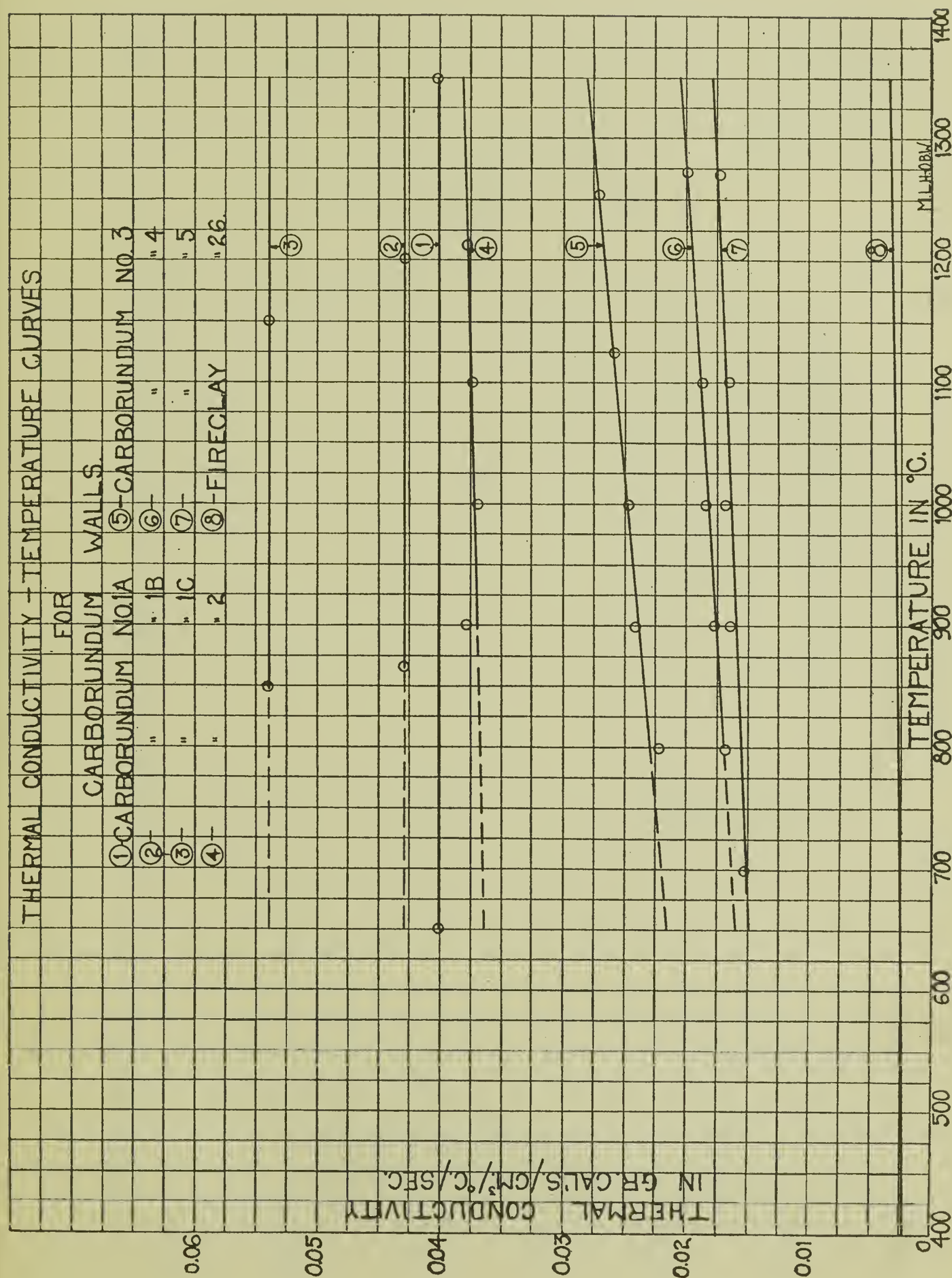

THERMAL CONDUCTIVITY - TEMPERATURE CURVES
FOR
CARBORUNDUM WALLS.
① CARBORUNDUM NO.1A
② " " 1B
③ " " 1C
④ " " 2
⑤ - CARBORUNDUM NO. 3
⑥ - " " 4
⑦ - " " 5
⑧ - FIRECLAY " 26
THERMAL CONDUCTIVITY IN GR. CALS./CM³/°C/SEC.
0.06
0.05
0.04
0.03
0.02
0.01
0
400
500
600
700
800
900
1000
1100
1200
1300
1400
TEMPERATURE IN °C.
M.L.HOBK.

Fig. 9.

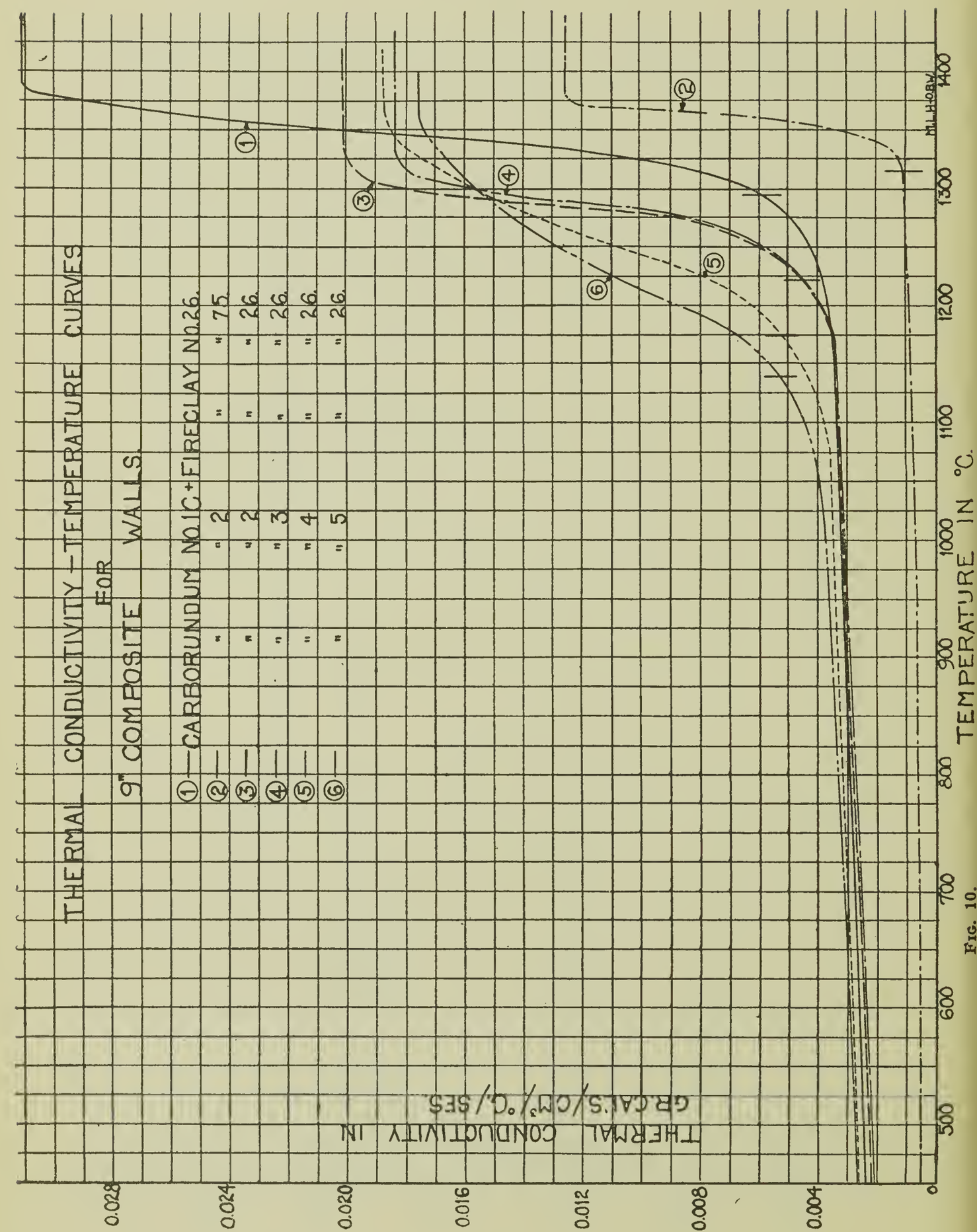

THERMAL CONDUCTIVITY—TEMPERATURE CURVES
FOR
9" COMPOSITE WALLS.
① — CARBORUNDUM NO.1C + FIRECLAY NO.26.
② — " 2 " " 75
③ — " 2 " " 26
④ — " 3 " " 26
⑤ — " 4 " " 26
⑥ — " 5 " " 26
THERMAL CONDUCTIVITY IN GR.CALS./CM³/°C./SES.
0.028
0.024
0.020
0.016
0.012
0.008
0.004
0
500
600
700
800
900
1000
1100
1200
1300
1400
TEMPERATURE IN °C.

Fig. 10.

The results on single and composite walls are shown in Table III. The curves showing the change in thermal conductivity with temperature are shown in Fig. 9, 10 and 11. It will be noted in Fig. 9 that the thermal conductivity for carborundum bricks does not change rapidly with temperatures. With the practically pure carborundum refractory, the thermal conductivity is constant at temperatures from 650° to 1,350° C.

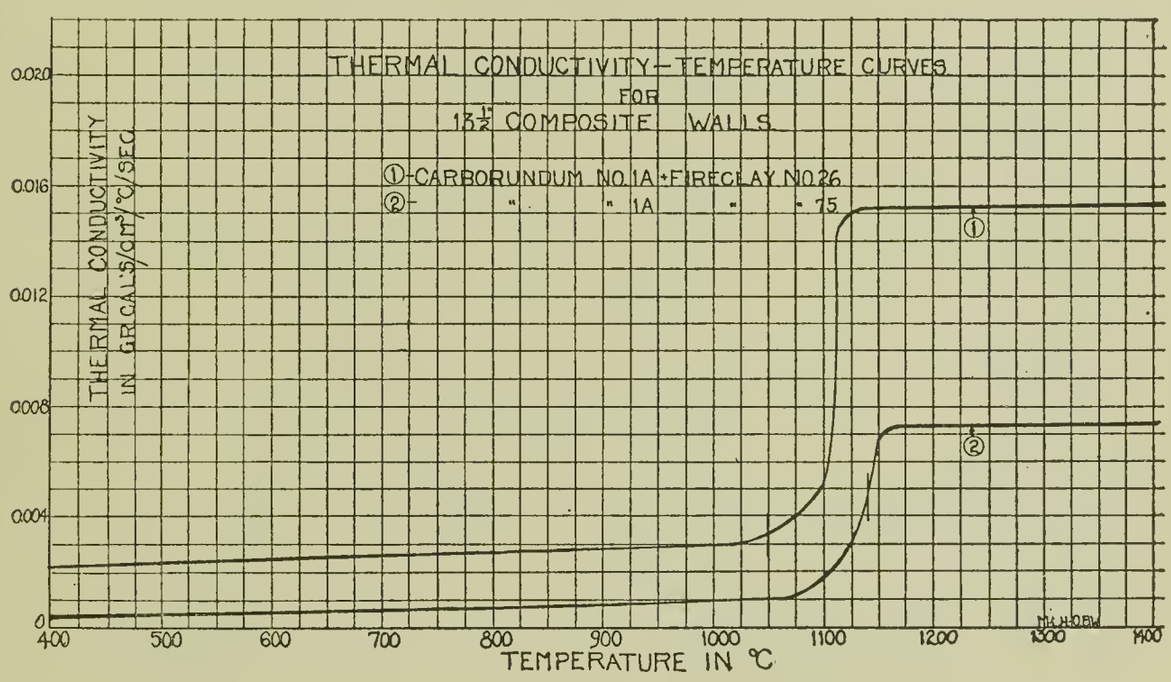


Fig. 11.

We believe that the high values for the carborundum brick, No. 1C, are due to gas diffusion outward toward the calorimeter. The surface of this wall on the fire side was not coated with cement, as in the case with the other walls. Attention has been called by Howe[14] to the abnormal effects on thermal conductivities due to penetration of hot gases through the refractories.

In order to determine the relation between the thermal conductivity at a given temperature and the percentage of silicon carbide in the carborundum bricks, it was necessary to consider the effect of the porosity of the brick. In the case of the fireclay bricks with 26 per cent and 74 per cent porosities it was found that the thermal conductivity at 1,350° C. was approximately inversely proportional to the porosity. With the assumption that the same relation would hold for carborundum bricks the thermal conductivities at

[14] Howe and Phelps, Jour. Amer. Cer. Soc., 5, 420 (1922).

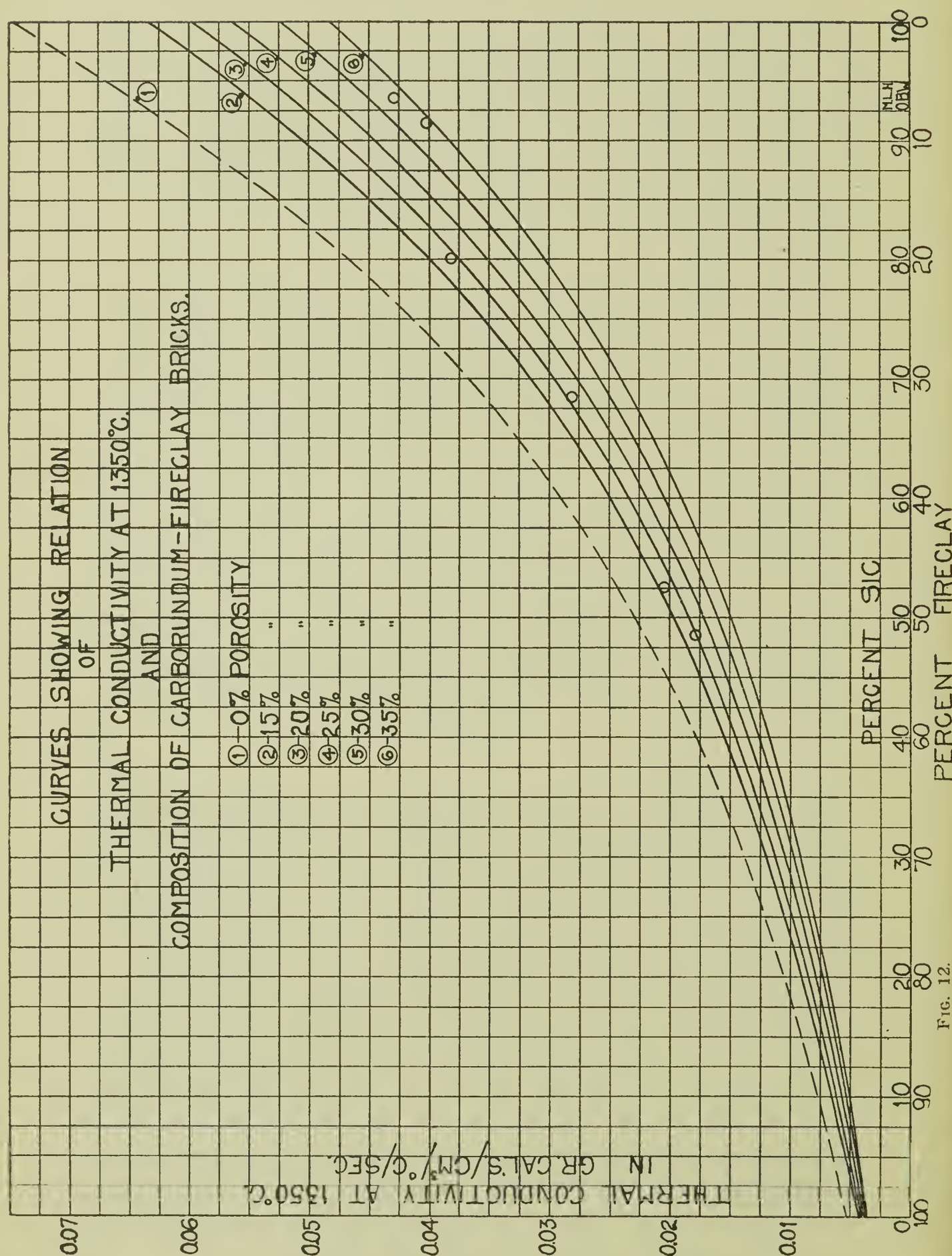

CURVES SHOWING RELATION
OF
THERMAL CONDUCTIVITY AT 1350°C.
AND
COMPOSITION OF CARBORUNDUM-FIRECLAY BRICKS.
①-0% POROSITY
②-15% "
③-20% "
④-25% "
⑤-30% "
⑥-35% "
THERMAL CONDUCTIVITY AT 1350°C
IN GR.CAL.S/CM³/°C/SEC.
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
PERCENT SIC
PERCENT FIRECLAY
100 0
90 10
80 20
70 30
60 40
50 50
40 60
30 70
20 80
10 90
0 100

Fig. 12.

1,350° C. for the uninsulated walls were calculated for 0 per cent porosity, and finally for 15, 20, 25, 30 and 35 per cent porosity, as shown in Table IV. Fig. 12 shows the change in conductivity with increased percentages of carborundum for these porosities.

TABLE III.

Thermal Conductivity of Carborundum and Composite Walls.

Carborundum Wall	Insulation	Per Cent SiC	Av. Heat Flow Gm. cal./ sq. cm. /sec.	Temp. Gradient at 1350° C. ° C./cm.	Ther. Cond. of Carbo. Wall at 1350° C. Gm. cal./ cu. cm./ ° C./sec.
9* in. Carbo. No. 1A	None	91.51	1.415	35.2	0.0403
9 in. Carbo. No. 1A	4.5 in. Fireclay No. 26	91.51	0.215	14.0	0.0153
9 in. Carbo. No. 1A	4.5 in. Fireclay No. 75	91.51	0.075	10.1	0.0074
4.5 in. Carbo. No. 1B	None	93.20	1.801	41.9	0.0430
4.5 in. Carbo. No. 1C	None	93.20	2.314	42.7	0.0542
4.5 in. Carbo. No. 1C	4.5 in. Fireclay No. 26	93.20	0.293	9.4	0.0314
4.5 in. Carbo. No. 2	None	80.10	2.170	56.8	0.0382
4.5 in. Carbo. No. 2	4.5 in. Fireclay No. 26	80.10	0.241	12.0	0.0201
4.5 in. Carbo. No. 2	4.5 in. Fireclay No. 75	80.10	0.074	5.8	0.0127
4.5 in. Carbo. No. 3	None	68.50	1.476	52.5	0.0281
4.5 in. Carbo. No. 3	4.5 in. Fireclay No. 26	68.50	0.254	13.8	0.0184
4.5 in. Carbo. No. 4	None	52.60	1.269	62.2	0.0204
4.5 in. Carbo. No. 4	4.5 in. Fireclay No. 26	52.60	0.289	15.4	0.0187
4.5 in. Carbo. No. 5	None	48.35	1.369	77.0	0.0178
4.5 in. Carbo. No. 5	4.5 in. Fireclay No. 26	48.35	0.302	17.0	0.0176

* 9 in. = 22.9 cm.

Fig. 10 and 11 show the very rapid rise in thermal conductivity in the carborundum portion of the composite walls. In comparing the thermal conductivities of the single and insulated carborundum walls, in Table III, it is noted that there is a marked decrease in the conductivity at a given temperature when the carborundum is insulated. This indicates that the conductivity is related to the heat flow or temperature gradient.

Fig. 13 shows the relationship between the thermal conductivity at 1,350° C. and the heat flow. It will be noted from these curves that in the case of single walls, where the temperature gradient is large, the change in conductivity with heat flow is small com-

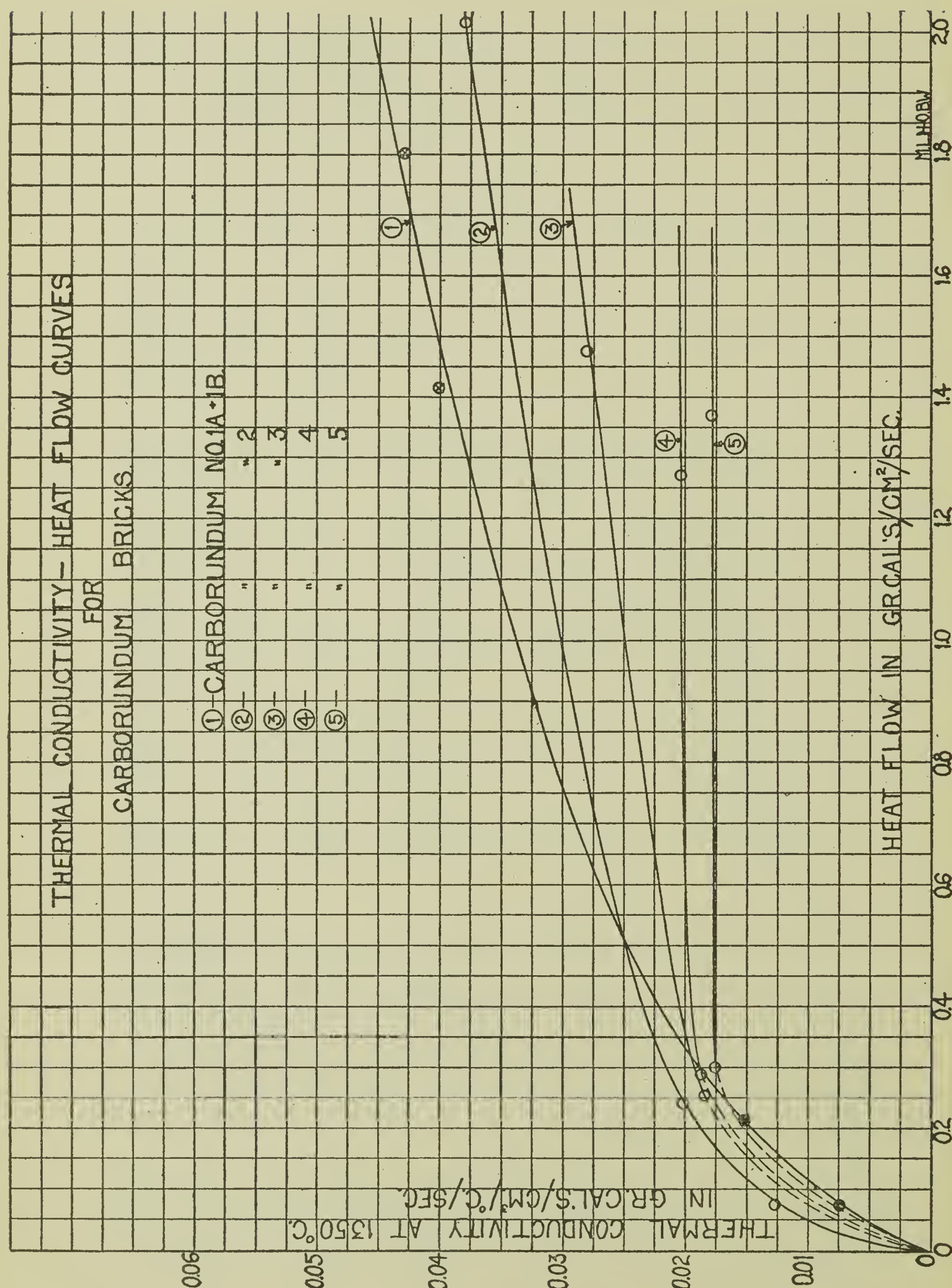

THERMAL CONDUCTIVITY - HEAT FLOW CURVES
FOR
CARBORUNDUM BRICKS.
①-CARBORUNDUM NO.1A+1B.
②- " 2
③- " 3
④- " 4
⑤- " 5
THERMAL CONDUCTIVITY AT 1350°C.
IN GR.CAL.S/CM²/°C/SEC.
HEAT FLOW IN GR.CAL.S/CM²/SEC.
MILHOBW
0.06
0.05
0.04
0.03
0.02
0.01
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0

Fig. 13.

pared to that in case of composite walls. The conclusion to be drawn from this is that thermal conductivity data for carborundum, obtained with large temperature gradients, is only applicable in furnace walls where similar conditions are present. With

TABLE IV.

Thermal Conductivity at 1,350° *C.*

Single Wall	Per Cent SiC	Per Cent Porosity	Experimental Value	Calc. for 0 Per Cent Porosity	Calc. for 15 Per Cent Porosity	Calc. for 20 Per Cent Porosity	Calc. for 25 Per Cent Porosity	Calc. for 30 Per Cent Porosity	Calc. for 35 Per Cent Porosity
Carbo No. 1A	91.51	34.1	0.0403	0.0649	0.0552	0.0519	0.0487	0.0454	0.0422
Carbo. No. 1B	93.20	33.8	0.0430	0.0611	0.0519	0.0489	0.0458	0.0428	0.0397
Carbo. No. 2..	80.10	18.4	0.0382	0.0468	0.0398	0.0374	0.0351	0.0328	0.0304
Carbo. No. 3..	68.10	20.7	0.0281	0.0354	0.0301	0.0284	0.0266	0.0248	0.0230
Carbo. No. 4..	52.60	17.7	0.0204	0.0248	0.0211	0.0198	0.0186	0.0174	0.0161
Carbo. No. 5..	48.35	18.9	0.0178	0.0219	0.0187	0.0176	0.0165	0.0154	0.0143
Fireclay No. 26	.....	26.8	0.0038	0.0052	0.0044	0.0041	0.0039	0.0036	0.0034

highly insulated walls the effect of the temperature gradient on the thermal conductivity should be taken in consideration. This added variable in the calculation of heat balances will, of course, complicate furnace problems, but it is of such a magnitude in the case of carborundum that it can not be neglected.

In using thermal conductivity data in these problems the question of surface and joint resistance to heat flow in the walls has often been raised. It is expected that the joint resistances of various walls would be approximately the same, but gas-film resistance at the inside surfaces would be quite variable in different installations, depending chiefly upon the velocity of the gases in the furnaces. In our experimental work the velocity of the gases was kept approximately constant, but the temperature at that hot surface was measured in only one wall. The temperature of the gases in the combustion chamber is not the same as that at the surface of the bricks, unless the heat flow through all

the furnace walls is uniform. In the tests on the single walls the heat flow through the test wall was several times greater than that through the furnace walls, so the temperature at the surface of the test wall was considerably lower than that of the furnace gases. The average difference between the temperature at the surface from the curves, Fig. 6, and that of the gases was found to be 260° C.

In the case of the composite walls, the heat flow through the test wall was approximately the same as that through the furnace walls, so that the average difference between the temperatures at the surface from the curves in Fig. 7 and that of the gases was approximately 80° C. To confirm this calculation a test was carried out on a 11 cm. fireclay wall, and the temperature drop at the hot surface of the bricks was measured. This was done by drilling a 3 mm. hole through the last 6 mm. of the brick, in the center temperature gradient hole, and inserting a Pt-Rd thermocouple with 3 mm. insulators into the hole until the junction was even with the surface of the brick. The temperature gradient curve obtained as in a regular test was then extrapolated to the hot surface of the brick, and the difference in the two surface temperatures thus obtained was the measure of the surface resistance. The temperature drop at the fireclay surface was found by this method to be 95° C.

The joint resistance between the carborundum and the insulation in the 23 cm. composite walls was determined by extrapolating the temperature gradient curves in each wall to the joint. The average drop due to this joint resistance was found to be approximately 30° C. This agrees with the results obtained by F. T. Snyder,[15] regarding the comparatively low temperature drop at the joints at high temperatures. In calculating the resistance to heat flow through composite furnace walls, the assumption may therefore be made that the temperature drop at the hot surface is approximately 80° C. and that at each joint is 30° C.

CONCLUSIONS.

In addition to the numerical values for the thermal conductivity of carborundum refractories, containing various percentages of silicon carbide and fireclay, we can draw from the data the following conclusions:

[15] Snyder, Trans. Am. Electrochem. Soc., **18**, 235 (1910).

1. The thermal conductivity of practically pure carborundum is constant for temperatures ranging from 650° C. to 1,350° C.

2. The thermal conductivity of ceramically bonded carborundum increases with increasing temperature.

3. The thermal conductivity of carborundum refractories decreases with the increase in percentage of fireclay bond.

4. The temperature gradient through a carborundum wall increases with the increase in percentage of fireclay bond in the bricks.

5. The thermal conductivity of fireclay is, approximately, inversely proportional to the porosity.

6. At any given temperature the thermal conductivity of carborundum increases as the amount of heat energy transmitted is increased.

7. At any given temperature the thermal conductivity of the fireclay is practically independent of the amount of heat energy transmitted within the range investigated.

8. The temperature drop, due to the gas-film resistance at the hot surface of insulated furnace walls is approximately 80° C. under these experimental conditions.

9. The temperature drop, due to the joint resistance in composite furnace walls, is approximately 30° C. under these experimental conditions.

DISCUSSION.

A. E. R. WESTMAN[16]: I think that Mr. Westmont should tell us why he obtained his values for the thermal conductivity of carborundum brick below 850° C. by extrapolating his curves in Fig. 9, rather than by calculating them from his actual readings as shown in Fig. 6, which would obviously give much lower results.

J. KELLEHER[17]: Mr. Westmont refers to the porosity of bricks. You could have one pore in the brick or several million pores for the same exterior size of the brick. Does not the size of the pore

[16] Dept. of Ceramic Eng., Univ. of Illinois, Urbana, Ill.
[17] Elec. Engr., FitzGerald Labs., Niagara Falls, N. Y.

affect the heat conductivity of the brick considerably? A special form of heat insulating bricks is on the market today, some bricks with small pores and others with large pores, and they act slightly differently. Has Mr. Westmont investigated that matter? Has Mr. Westmont investigated the re-crystallized carborundum refractories besides the bonded, and whether there is a difference in the heat conductivity through a re-crystallized carborundum brick in the direction of the grain growth and across the grain growth.

O. B. Westmont: In connection with the question of measuring the temperature gradient in the inch (2.54 cm.) of refractory wall directly under the calorimeter, the temperatures recorded near the surface of the wall were undoubtedly lower than the true temperatures of the brick, due to convection currents and gas films in the gradient holes and protection tubes. The temperatures in the main portion of the brick as recorded were, however, found to be within approximately 5° C. of the temperature of the brick by the tests described on page 490. In the tests on the 23 cm. (9 in.) carborundum walls it was found, on the basis of the temperature gradient curve (Fig. 8, Curve 1), that the thermal conductivity was constant between 650 and 1350° C. (Fig. 9, Curve 1). Since there was no change in the conductivity from 650 to 850° C. in this case, it seemed advisable to extrapolate the curves over the range in question in the 11 cm. (4.5 in.) walls, where there was such an element of doubt in the actual temperature measurements.

Regarding the porosity of refractories, we have found with fireclay bricks having porosities identical within one per cent that the thermal conductivity was increased over 38 per cent by increasing the size of pores a few diameters. With large pores in the refractory, the heat transferred by radiation and convection becomes a very important factor in thermal conductivity measurements.

As regards re-crystallized carborundum refractories, it is probable that the conductivity would vary to some extent with the direction of grain growth. In our actual experiments, however, no attempt was made to control this factor, the bricks being selected to represent the general run of our product and laid as they would be in commercial installations. In loading the re-crys-

tallization furnace, no attempt is made to place the bricks in a definite position relative to the core.

J. KELLEHER: As regards the recrystallized carborundum wall, were these bricks laid on the flat, that is, was the wall built of bricks lying flat?

O. B. WESTMONT: Yes.

J. KELLEHER: And that was the way they were lying in the recrystallization furnace during re-crystallizing relative to the core.

A paper presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 3, 1924, Mr. F. A. J. FitzGerald in the Chair.

PREPARATION OF ARTIFICIAL SILLIMANITE FOR REFRACTORY USES.[1]

By Clarence E. Sims,[2] Hewitt Wilson[3] and Henry C. Fisher.[4]

Abstract.

The experimental work leading to the adoption of a furnace for the preparation of artificial sillimanite is described. Clay was found to be peculiarly difficult to melt, but could be reduced to sillimanite by elimination of the excess silica. Natural sillimanite has a different composition from the synthetic product. Artificial sillimanite containing excess silica is vitreous; that with excess alumina is stony. The latter form has excellent refractory properties as compared to silica and magnesite brick. Lime is a particularly undesirable impurity.

INTRODUCTION.

As part of its program of work on super-refractories, the Northwest Experiment Station, of the Bureau of Mines, working in co-operation with the University of Washington, took up the study of artificial sillimanite. Although it has been shown that the artificial compound of alumina and silica is not the same as the natural sillimanite, it has not been given a distinguishing name, but is widely known as sillimanite. Therefore, in this writing, it will be called artificial sillimanite to distinguish it from the mineral of that name. This material was chosen because it gave promise of having properties approaching those of an ideal refractory. Being an aluminum silicate, it is composed of two of the earth's most common oxides, and should possibly be resistant

[1] Manuscript received August 16, 1924. Published by permission of the Director, U. S. Bureau of Mines.

[2] [3] [4] Electrometallurgist, Consulting Ceramist, and "Fellow," respectively, Northwest Experiment Station, U. S. Bureau of Mines, at Seattle, Washington, in co-operation with College of Mines, University of Washington.

to both acid and basic slags. It has a high melting point (1,816° C.) and, being crystalline, the melting point should be sharp and definite. It has a hardness of 6 to 7 and should, therefore, withstand abrasion.

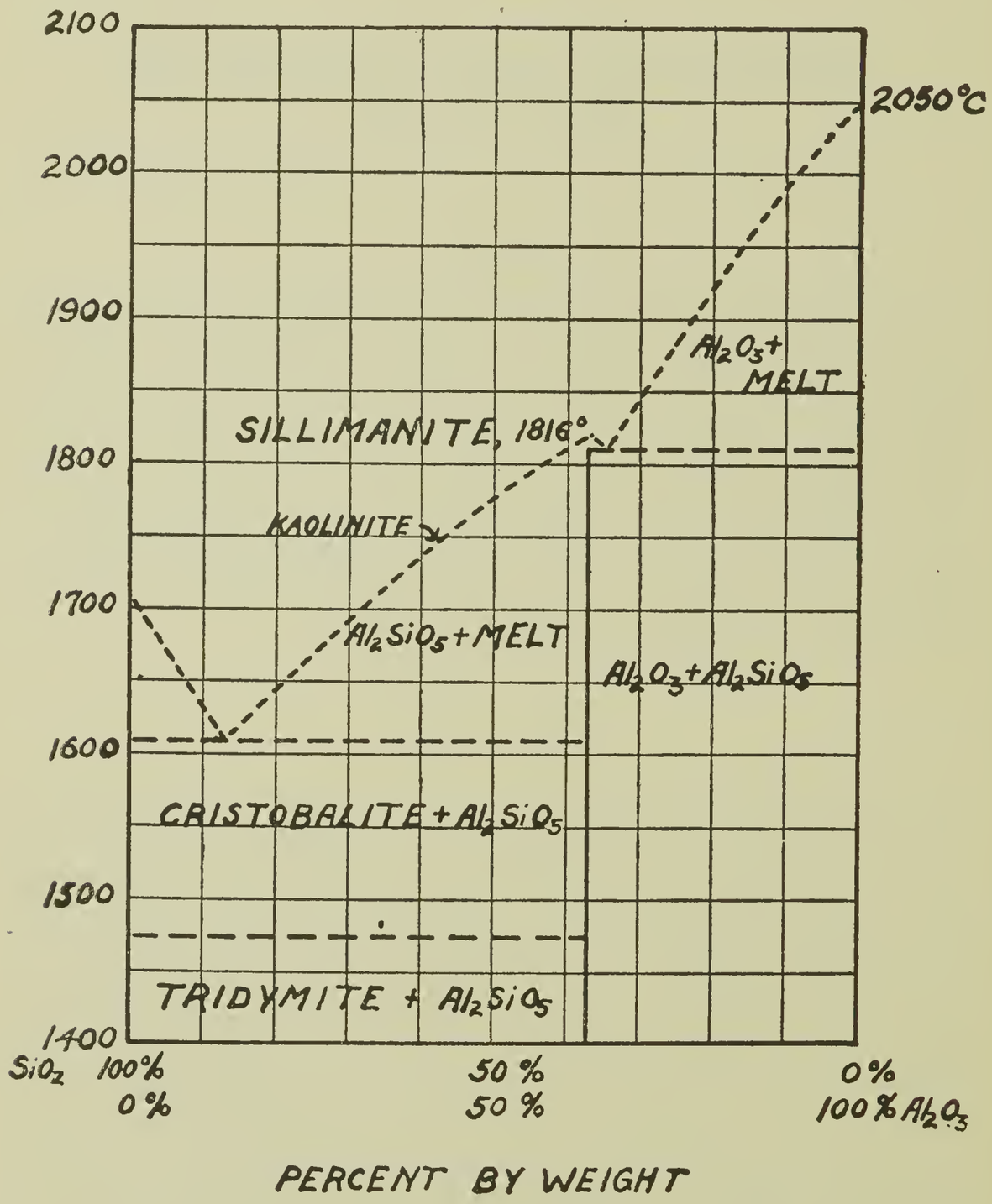


FIG. 1. Silica-Alumina Diagram of Rankin and Wright (Incorrect).

Mineralogically, natural sillimanite belongs to the andalusite group of minerals. The three members of this group are andalusite (chiastolite), sillimanite (fibrolite), and cyanite (kyanite

or disthene). These are all of the same composition and are well described by F. W. Clarke.[5]

Natural sillimanite is a definite chemical compound, Al_2O_3, SiO_2, containing 62.9 per cent alumina and 37.1 per cent silica. The silica-alumina concentration diagram worked out by Rankin and Wright, Fig. 1, was used as a basis for the experimental work. It shows only one compound, sillimanite, and a eutectic on either side, one with silica, and the other with alumina. This diagram is

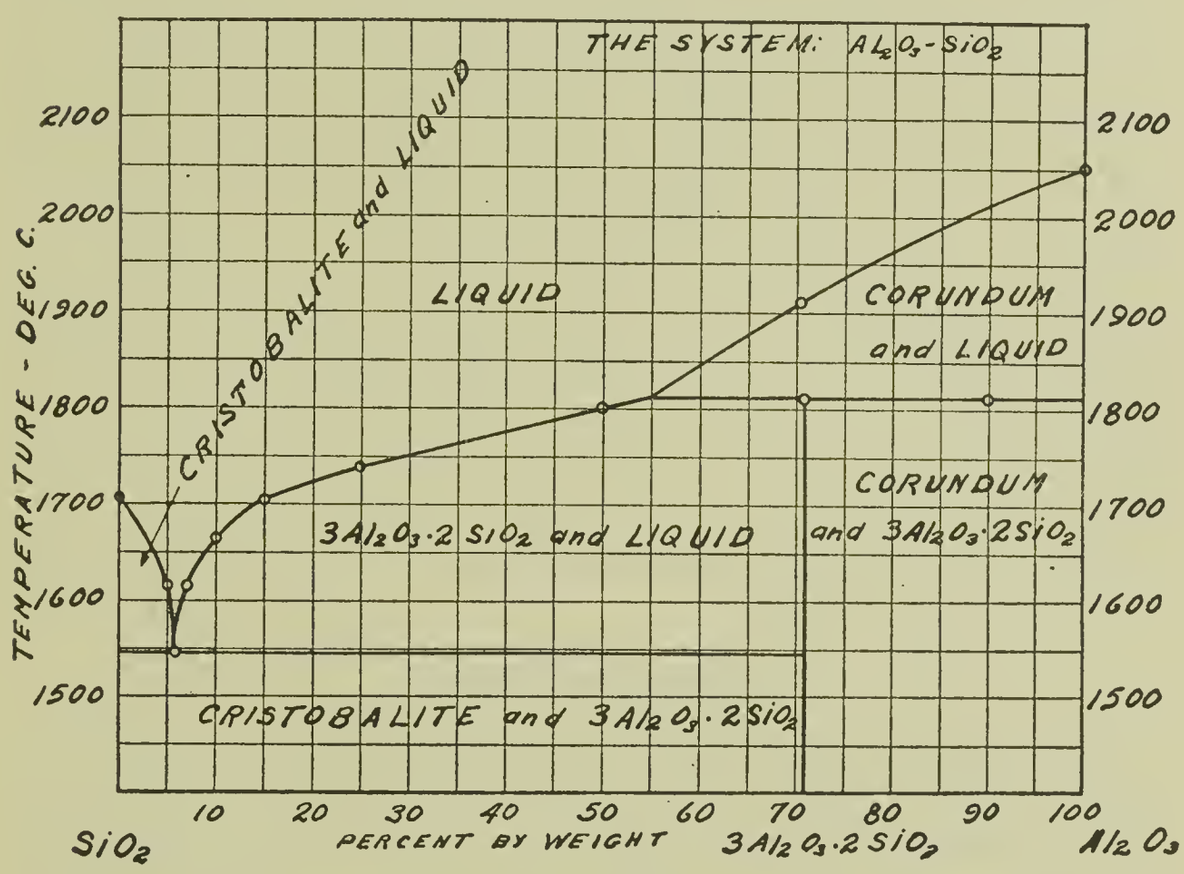


FIG. 2. Silica-Alumina Diagram of Bowen and Greig (Correct).

incorrect, as was found later by Bowen and Greig,[6] who have substituted the diagram shown in Fig. 2. Although the new diagram had no effect on the results obtained, it does help to explain some of the phenomena observed, as will be discussed later.

Various investigators have found sillimanite in porcelains, glazes, paving brick, and in Seger-Orton cones. In fact, it seems to form whenever silica and alumina react at high temperatures.

[5] Clarke, F. W., Data of Geochemistry: U. S. Geol. Survey Bull., 616 (1916), p. 409.

[6] Bowen, N. L., and Greig, J. W., The system $Al_2O_3 . SiO_2$. Am. Ceram. Soc., 7, 238 (1924).

ARTIFICIAL SILLIMANITE.

Noel Lecesne[7,8,9,10] used a coke-fired furnace with an air blast, and A. Malinovszky[11] used the same type of furnace to fuse clays mixed with coke, iron, and cryolite. Microscopic examination of the latter's product showed well-developed sillimanite crystals embedded in a ground mass of glass.

Raw Materials.

The raw materials from which sillimanite can be produced are mainly bauxite, diaspore, gibbsite, and kaolin, or mixtures of these. The various clays are, of course, the most plentiful and cheapest source of aluminum silicates, but there are numerous deposits of bauxite and diaspore, not suited to the production of aluminum, that are thoroughly satisfactory as a raw material for sillimanite. Practically all clays contain too much silica, pure kaolin ($Al_2O_3.2SiO_2.2H_2O$) containing three times too much. Starting with clay, the correct composition may be obtained either by augmenting the alumina content with the addition of some high-aluminous material, or by removing the excess silica by reduction with carbon. There being no known materials in the Pacific Northwest richer in alumina than the clays, the latter procedure is of importance.

Experimental Fusions.

The early experiments of this investigation consisted mainly of search for the most efficient methods of melting the materials to produce sillimanite, and means of removing certain undesirable impurities. Because of the high temperature required, no other heating medium than the electric current was considered.

The first furnace consisted of an upright, cylindrical steel shell, open at both ends and supported on a fire-brick base. One electrode came through the base and projected an inch or two. The other was suspended directly above the bottom electrode, and centered as regards the shell. It had a capacity of 22 to 45 kg.

[7] Lecesne, Noel, Manufacturing refractory materials with fused bauxite: Trans. Eng. Ceram. Soc., 17, 192 (1917-1918).

[8] Bigot, A., On the new refractory and abrasive matter called corindite: Trans. Eng. Ceram. Soc., 17, 267 (1917-1918).

[9] French patent No. 471,513, July 11, 1914.

[10] English patent No. 17,289, 1916.

[11] Malinovszky, A., The Malinite process for the production of sillimanite refractories: Jour. Am. Ceram. Soc., 3, 40 (1920).

(50 to 100 lb.) of charge. No permanent lining was provided, an unmelted layer of charge next to the shell serving the purpose. The radiation from the air-cooled shell usually prevented this layer from fusing. When that was insufficient, a water spray from a hose was turned on the shell. The furnace was designed to start as an indirect-arc furnace, and, as soon as a bath was formed, to operate as a direct-arc furnace. The charge consisted of calcined china clay, mixed with varying proportions of carbon. The carbon was expected to remove part of the silica by reduction according to the following reactions:

$$SiO_2 + C \rightarrow SiO + CO$$

or

$$SiO_2 + 2C \rightarrow Si + 2CO$$

Both of these reactions took place. During fusion and reduction great volumes of gas were evolved. This gas consisted of CO and SiO, and burned at the surface of the charge with an intensely brilliant flame, forming a dense white fume. Impure globules of metallic silicon were found in the fused mass. Good reductions were obtained, the alumina content of 42 per cent in the calcined clay being increased in some cases to 70 per cent in the fused material.

Although both fusion and reduction were accomplished, this furnace was far from being satisfactory. However, owing to the nature of the material being treated, some trouble would be encountered in any type of furnace. Clay is practically non-conductive below the melting point and has a very low conductivity even when molten. Instead of a definite melting point, it has a long softening range, where it acts as a viscous liquid. In the operation of the furnace a little of the unfused clay falling between the electrodes would break the arc. The arc could be broken in other ways, and if it was not immediately re-established, the fusion would chill slightly and become non-conductive, making it difficult or impossible again to start an arc.

The molten clay was not sufficiently conductive to act as an electrode; the arc from the upper electrode apparently cast it aside and penetrated to the lower graphite electrode. Because of its heat insulating quality, the clay exposed to the arc was not only melted, but actually vaporized, while that a half-inch back

from the exposed surface was only sintered. The gases evolved (mainly CO and SiO) escaped through the porous charge above, and being very hot, they sintered the clay through which they passed, welding it into large masses, which bridged over and failed to feed down into the melting zone. This sintering of the clay rendered it non-porous, and the hot gases rushing with great velocity through the small openings melted out pipes.

The reduction of silica by solid carbon took place, of course, in the molten clay, and the gases being thus liberated in the liquid phase carried considerable amounts of molten material to be built

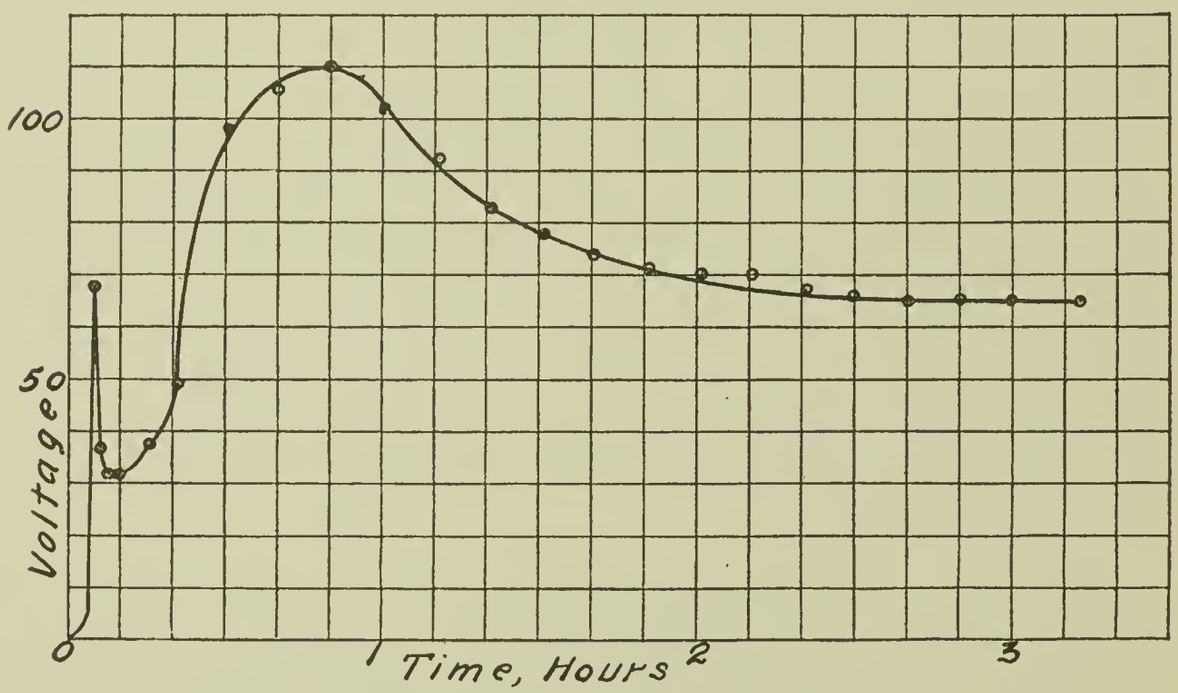


FIG. 4. Furnace Voltage. Power input kept constant.

into miniature lava cones at the surface or spattered about. The sintering of the charge would finally freeze the upper electrode immovably fast and force the discontinuance of the run. This was the usual performance of this furnace and caused a small yield and large power consumption. When melting diaspore, which has a sharper melting point, these troubles largely disappeared and the melt progressed smoothly.

A resistance furnace of the carborundum type was tried using a train of ground graphite as a core. As soon as the clay about the core started to melt, reduction also began, and the evolved gases caused first a swelling and then an eruption of the molten clay. This action disrupted the carbon train and stopped the flow

of current. A solid core in the shape of a graphite rod was substituted for the granular train. The current was then maintained until the action of the clay on the incandescent carbon burned it apart, breaking the circuit suddenly. Although the voltage was rapidly increased to 500 volts, current would no longer flow.

After several other types of furnaces were tried, the information gained led to the adoption of the furnace shown in Fig. 3. It was merely a hollow steel shell placed on a foundation of silica brick. Two 75 mm. (3-in.) graphite electrodes were suspended above from water-cooled holders. These holders, insulated from each other, were held rigidly together so that the electrodes moved in unison, with a constant distance of four inches between them.

In starting this furnace a 15 cm. (6-in.) layer of the charge was first tamped firmly in the bottom. The electrodes, of equal length, were lowered to touch the charge. A piece of paper was wrapped around the lower ends of the electrodes, as a belt around two pulleys, and the space inside the paper was filled with granular carbon. More of the charge crushed to 2 in. or less was added, until the shell was full. The operating characteristics of the furnace, where the voltage was varied to maintain a constant power input, are shown by the curve in Fig. 4.

At first the carbon train was cold and had a high resistance, but, as it rapidly heated, the resistance decreased to a minimum point. The hot carbon melted the surrounding clay, which flowed in and gradually replaced it. The molten clay, while also an electrical conductor, is much less conductive than the carbon, and, in consequence, the resistance increased again to a maximum point when the carbon had all been replaced. During this replacement the power fluctuated badly and, if contact through the charge was lost, it was difficult and sometimes impossible to regain. This made close attention from the operator necessary.

As the melt progressed and the temperature and cross-section of the molten bath increased, the resistance decreased correspondingly. The formation of an arc was avoided as much as possible, thus eliminating any small areas of intense temperature. The heat was transferred to the unfused clay more by convection currents than by radiation or conduction. The same troubles with clay were encountered in this furnace as were met in the arc

furnace, but to such a small degree that they were easily controlled. At times the melt threatened to fuse its way through the shell, but a water spray from a hose, applied as soon as a bright red spot appeared on the shell, stopped such action.

When simple melting without reduction was being conducted, the difficulties were reduced to a minimum, and the furnace could be highly powered for rapid melting. But when reduction was also being conducted, the furnace was operated so that the evolved

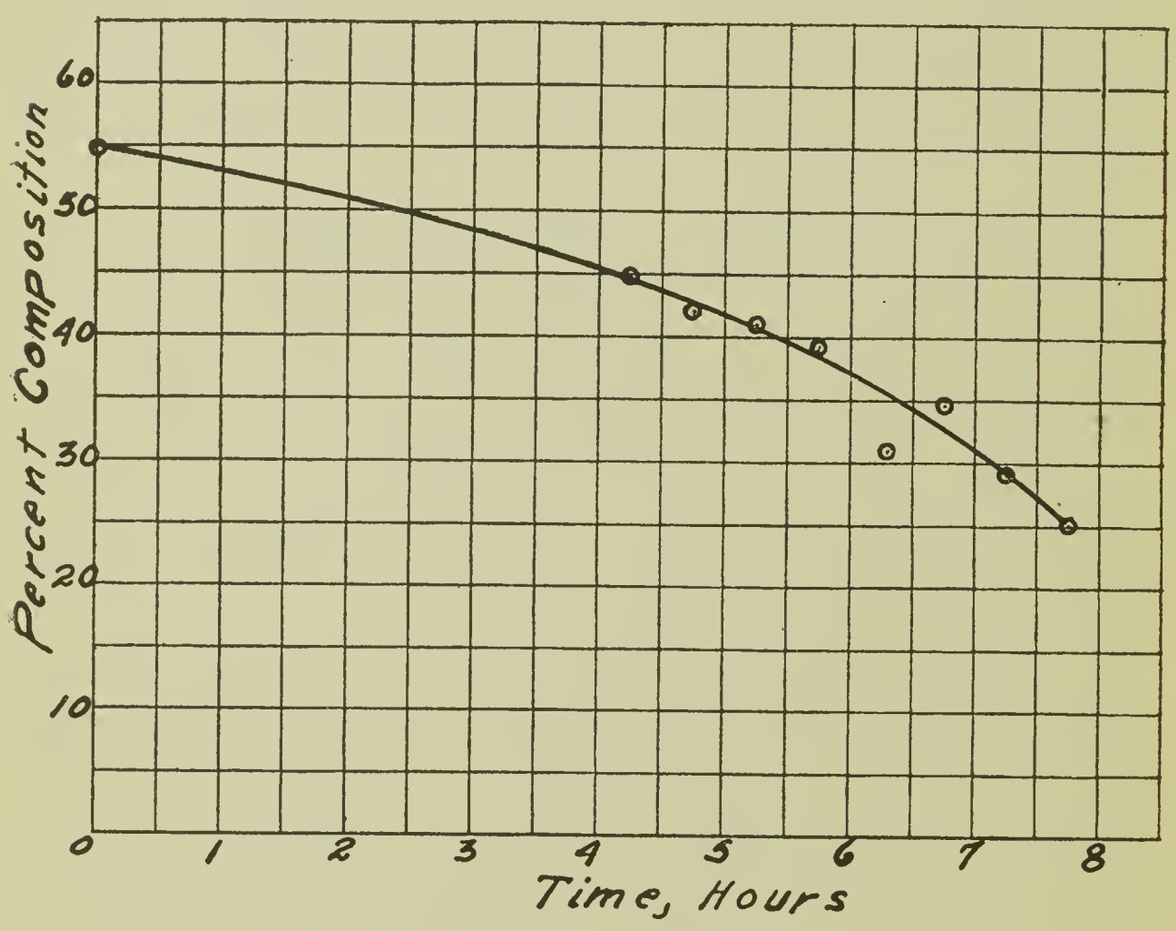


FIG. 5. Drop in Silica Content as the melt progressed.

gases had time to escape quietly, and without blowing out the molten material. The melting operation was facilitated by calcining the clay material before fusing. The charge did not settle evenly in the furnace, but bridged and then suddenly dropped; if raw material containing water was suddenly precipitated into the molten mass, the water was expelled with almost explosive violence.

When reduction of silica was being carried on during melting, it was found helpful to add sawdust to the charge to keep it

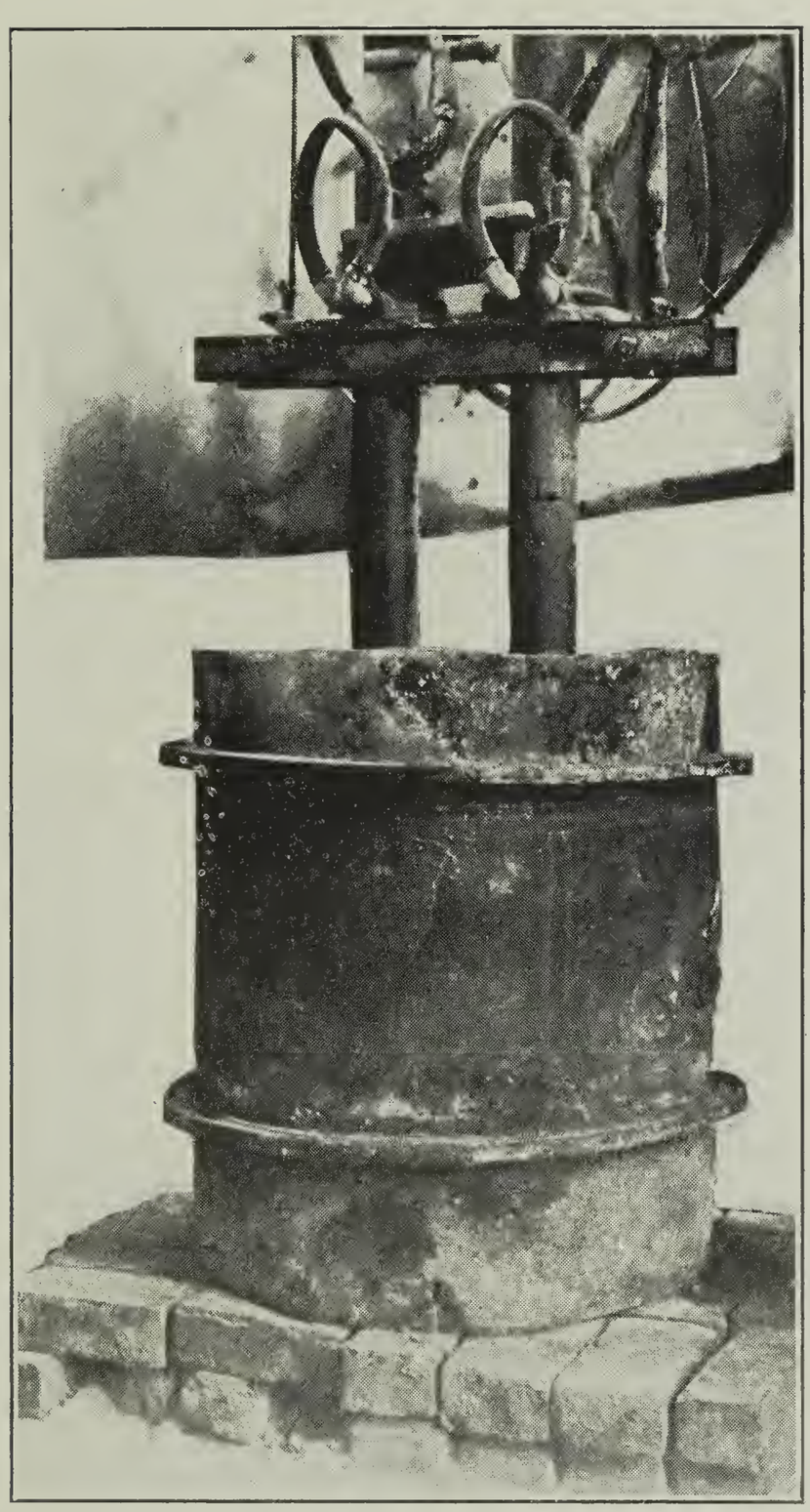
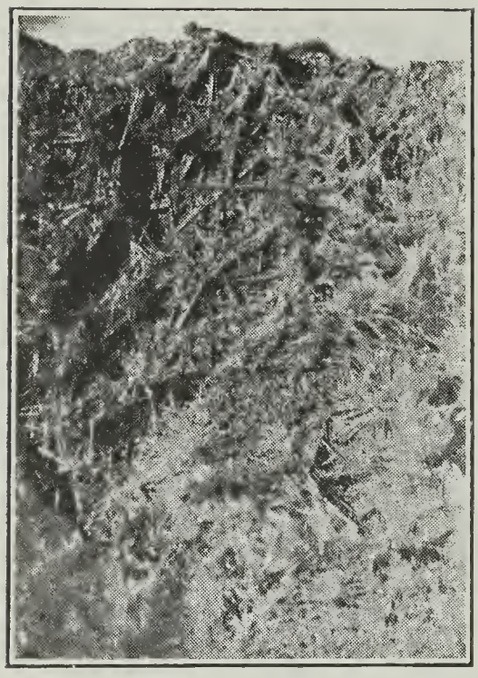
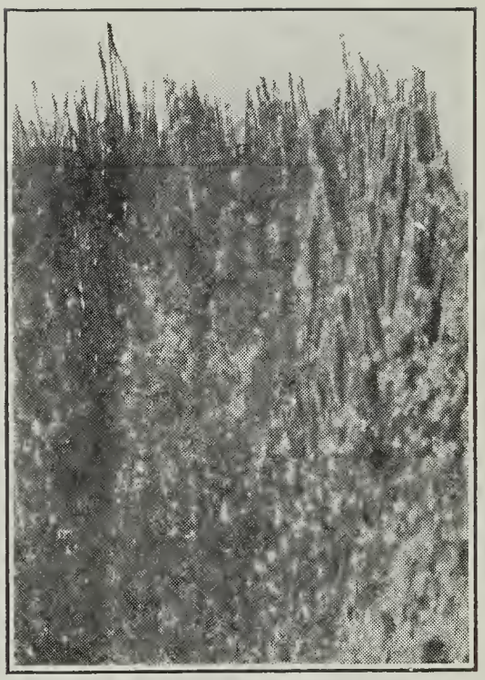


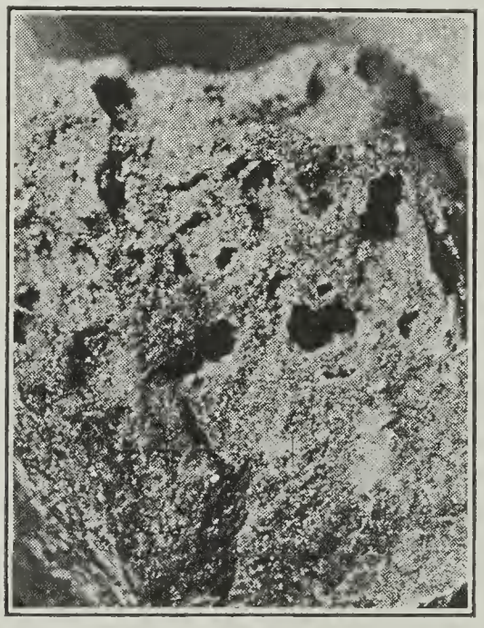
Fig. 3. Electric furnace for making fusions.



(a) Radial crystals.



(b) Parallel crystals.

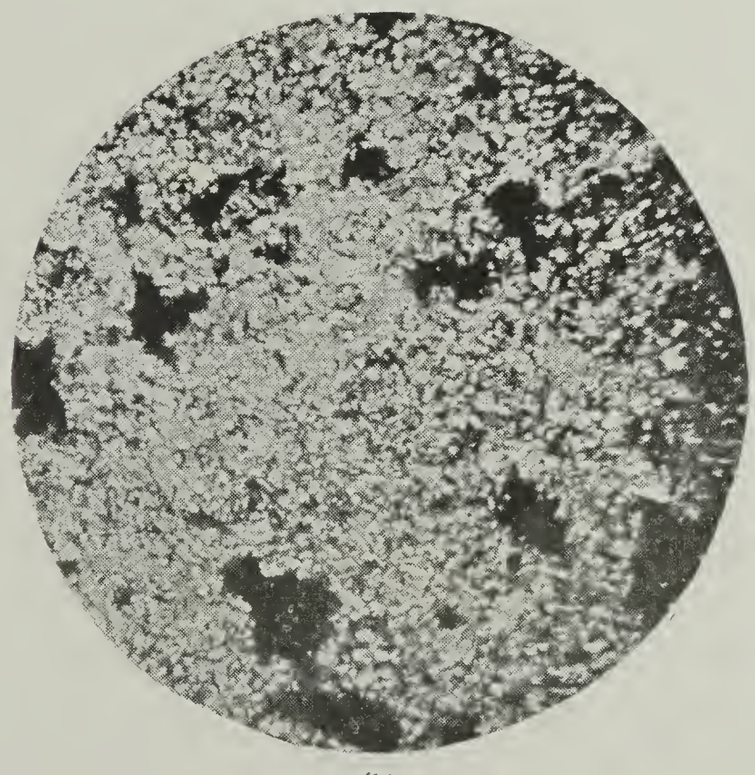


(c) Stony.

FIG. 6. Artificial Sillimanite.

The habits in which artificial sillimanite crystallizes.
(a) and (b) Sillimanite containing excess silica.
(c) Sillimanite containing excess alumina.

(a)



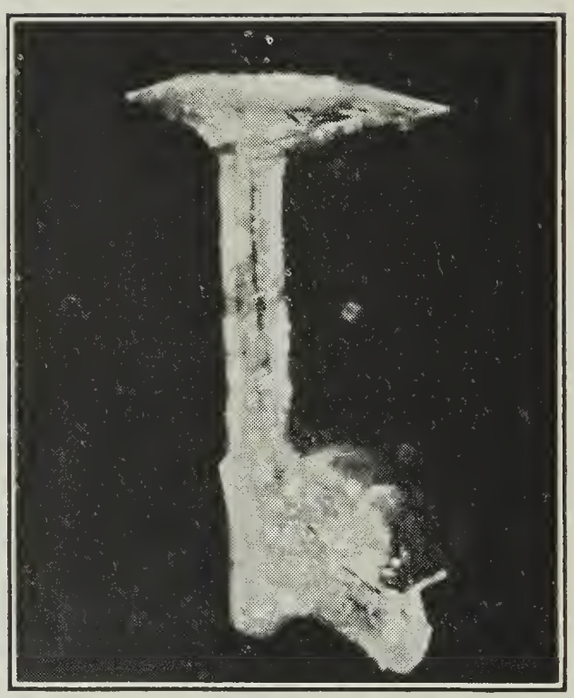
(b)

Fig. 7.

Photomicrographs of thin sections of artificial sillimanite.

(a) Containing excess silica.

(b) Containing slight excess of alumina.



(a)

(b)

FIG. 8. Sillimanite.

Needle-like crystals of sillimanite stopped in its growth by a hexagonal plate of corundum. No example was found where a sillimanite crystal penetrated a corundum crystal, and the interference with the growth of the former was evident. Magnified about 35 diameters.

porous and facilitate the escape of the gases. When charcoal was substituted for coke as a reducing agent, even better results were obtained and the use of sawdust was unnecessary.

There was always some reduction of silica during melting, even though no effort was made toward that end. Just the carbon train used in starting the fusion and the action of the electrodes reduced the silica content about 2 per cent. Most of the iron oxide present in a charge can readily be removed by the addition of carbon, while lime and magnesia are only slightly reduced by vaporization. Thus, a charge containing 12 per cent Fe_2O_3 yielded a fused product containing only 0.3 per cent FeO.

The reduced silicon and iron formed metallic globules of ferro-silicon, which contaminated the product. In a charge of low-iron content these metallic particles consisted mainly of silicon, with a small amount of aluminum. When this was the case, the specific gravity was so low that they did not readily settle out, but were disseminated throughout the fusion. The coefficient of expansion of these alloy particles was about the same as that of sillimanite, and after cooling they were welded fast and would not split away.

When the melt was broken up the cleavage was through the metallic particles and, therefore, it was impossible to free them mechanically from the sillimanite. When sillimanite containing such inclusions was made into brick and fired the metal oxidized, and the increase in volume disintegrated the brick.

The only satisfactory method found for handling these metallic inclusions was to add iron to the charge, preferably in the form of turnings or borings, although iron oxide and carbon have been used successfully. When the iron content of the metal was raised to equal the silicon, the specific gravity was increased, causing it to settle more rapidly, and the shrinkage in cooling became sufficient to cause the metal to form in loose pellets in cavities of the sillimanite. If the iron content was more than twice the silicon the alloy was magnetic enough to be picked out with a strong magnet.

When melting materials containing not more than 10 or 15 per cent silica in the presence of carbon, carbides were formed. These were probably aluminum and calcium carbides, and remained as inclusions in the fusion. When such material was made into brick, the moisture reacted with the carbide during drying and

caused the brick to puff up like a loaf of bread. Hot-water treatment of the crushed grog destroyed the carbide. With higher silica contents, such as used in making the artificial sillimanite, no trouble was experienced with carbide.

In reducing silica from clay to form sillimanite it is difficult to calculate definitely the amount of carbon necessary for reduction, because it is impossible to predict how much of the silica will be reduced to Si, and how much to SiO. Only half as much carbon is required to reduce silica to SiO as to Si. Likewise, the amount of iron needed to render the metal magnetic is dependent on the proportion of silica reduced to Si. These quantities can readily be determined by experimentation.

Using a flint clay of the composition,

SiO_2	Al_2O_3	FeO	CaO	MgO	H_2O
47.0	39.7	3.5	1.7	0.8	7.0

and reducing the silica content to approximately 30 per cent would require the elimination of 60 per cent of the silica, or 30 lb. per 100 lb. (13 kg. per 45 kg.) of clay. To reduce the silica to silicon and the iron oxide to metallic iron would require theoretically about 14 lb. (6.4 kg.) of carbon; yet 10 lb. (4.5 kg.) was found to be ample. However, it is desirable to have a small surplus of carbon to prevent excessive electrode consumption.

Fig. 5 shows how the silica content of the molten portion of a charge in a typical melt decreased as the melt progressed. When interpreting this curve, it should be borne in mind that the amount of fused material was constantly increasing by additions from the raw charge. Therefore, the actual decrease in silica was greater than is apparent from the slope of the curve.

The production of sillimanite by melting materials of such proportions of alumina and silica as to avoid the necessity of removing silica is, of course, the less difficult and more attractive operation. However, in situations where high-aluminous materials are costly and clay comparatively cheap, it may be more economical to use the clay alone. The latter will require considerably more power, necessitating also cheap power. In fact, the cost of power would probably be the deciding factor in determining which material would be used. Due to the loss of silica when only clay is used, a greater quantity of raw material would be needed than

when using bauxite and clay. To offset this it is possible to recover part of the reduced silica as ferrosilicon.

After the sillimanite is prepared the cost of making brick would then be comparable to that of silica brick, except that the firing would require a higher temperature for a somewhat longer time.

Characteristics.

One of the most noticeable properties of artificial sillimanite is a powerful tendency to crystallize. Even the rapidly-chilled samples showed well-developed crystals and the more slowly-cooled products often contained crystals over two inches in length. It crystallizes in two distinct habits, as shown in Fig. 6. The first of these has long, needle-like crystals with a vitreous luster and conchoidal fracture. Either they have no orientation, except a slight tendency toward radial formation as in (a), or are parallel as in (b), Fig. 6. The second (c) is stony, dull and almost microcrystalline, with slightly larger crystals of corundum lining the cavities.

Petrographic examination of the vitreous, coarsely-crystalline specimens showed them to consist mainly of sillimanite, with a matrix of glass having an index of refraction very close to tridymite. The amount of glass in some specimens was estimated to be as high as 25 per cent. The stony, finely-crystalline material, however, proved to be a mass of very small intergrown crystals of sillmanite and corundum with very little glass.

During the earlier work an effort was made to keep all melts close to the composition of natural sillimanite ($Al_2O_3.SiO_2$) and only vitreous products were obtained. Owing to the strong tendency of the artificial sillimanite to crystallize, the glass was thought to be caused by excess silica, but the fact that it occurred above the 1 to 1 ratio seemed to indicate that it was amorphous sillimanite. Moreover, the vitreous material gave such discouraging results on test as to make it appear useless as a refractory. When the experiments were carried further to include compositions higher in alumina, the stony sillimanite was obtained which gave an entirely new outlook to the whole investigation.

A series of melts with varying alumina contents showed a fairly sharp transition from the vitreous to the stony condition. One

melt, with only a few small crystals of corundum, but still vitreous and, therefore, on the dividing line, had the following composition.

	Per cent
Al_2O_3	68.0
SiO_2	28.0
FeO	1.1
CaO	1.7
MgO	0.6

All melts higher in alumina than this were stony, and all lower were vitreous. The transition point at this high-alumina content could not be satisfactorily explained by the diagram of Rankin and Wright, and it was thought that the impurities present changed the effective silica-alumina ratio by the formation of other compounds. But the work of Bowen and Greig[12] showed a different composition for the artificial aluminum silicate than had been assumed. In order to check his results on our own product, clean, protruding crystals of artificial sillimanite were picked from several melts and analyzed. The results are given in Table I and are in agreement with those of Bowen. The composition of artificial sillimanite, therefore, instead of being $Al_2O_3.SiO_2$ with a 63:37 ratio, is $3Al_2O_3.2SiO_2$ with a 72:28 ratio, and it is at approximately this latter ratio that the fused material changes from the vitreous to the stony form.

TABLE I.

Analyses of Artificial Sillimanite Crystals.

	Melt No. 9		Melt No. 66	
	Average melt	Clean crystals	Average melt	Clean crystals
Al_2O_3	60.0	70.0	60.0	69.0
SiO_2	36.4	28.3	37.2	28.2
FeO	...	0.6	0.3	0.5
CaO	...	1.8	1.9	2.2
MgO	...	0.6	0.4	0.3

The photomicrographs of thin sections in Fig. 7 show the great difference in structure, caused by excess of silica on the one hand and excess of alumina on the other. The reason for this difference

[12] Bowen, N. L., and Greig, J. W., The system $Al_2O_3.SiO_2$. Am. Ceram. Soc., 7, 238 (1924).

seems obvious from the diagram of Bowen and Greig. Starting with molten material with a composition slightly greater in silica than the 3 : 2 ratio, and allowing it to cool, we find that at 1,900° C. corundum starts to crystallize out, and continues until 1,810° C. is reached. At this point sillimanite ($3Al_2O_3.2SiO_2$) needles start to form, and the small corundum crystals are reabsorbed by the liquid. The sillimanite crystals continue to grow uninterrupted in a liquid medium, through the comparatively long range of 265°, or until the sillimanite-silica eutectic at 1,545° C. is reached.

On the other hand, when there is a small excess of alumina the corundum begins to crystallize around 1,900° C., but when 1,810° C. is reached it is not absorbed. There may be either a slight decrease or increase in the corundum at this point, depending on the amount that had previously crystallized out. Here the sillimanite crystallizes with all the characteristics of a eutectic and a definite freezing point. Added to this is the interference of the corundum crystals previously formed, with the growth of the sillimanite, as illustrated in Fig. 8. Naturally, with impure materials the transition point would not be sharp, and there will be melts exhibiting features of both the vitreous and stony forms.

Bowen and Greig's diagram also indicates that the 3 : 2 compound melts incongruently, breaking down to corundum and liquid. All the tests in the present investigation gave evidence of congruent melting at a definite temperature. Splinters of artificial sillimanite melted like a piece of ice. There was no softening or slumping, but the outside melted and ran away, leaving the inside intact and unchanged until exposed. There seems to be a discrepancy here, but returning to the diagram and following a 3 : 2 composition as it melts, we find that at 1,820° C., just 10 degrees above the melting point, this composition consists of two-thirds liquid and only one-third solid (corundum) under equilibrium conditions. Under conditions of rapid melting there would be even less corundum, not enough to affect the fluidity of the liquid. Therefore, although artificial sillimanite does melt incongruently, the fact can be disregarded for all practical considerations.

It is interesting, also, to follow through a 1 :1 composition. At 1,550° C., just above the melting point of the eutectic, there is

over 13 per cent liquid, at 1,800° C., 41 per cent liquid, and at 1,820° C., 84 per cent liquid.

Artificial sillimanite is not readily attacked by acids or alkali; even HF dissolves it very slowly. Fusion in sodium carbonate does not completely decompose it. Sodium peroxide or a mixture of sodium carbonate and borax glass are the only reagents found practical in making fusions for chemical analysis. This would indicate great resistivity to slag action.

Brick.

In making brick the fused product was crushed and passed over a magnetic concentrator, which removed the metallic inclusions and bits of iron from the crusher. It was then screen-sized and mixed according to the following formula:

	Per cent
Through 2-mesh on 4-mesh	50
Through 20-mesh	40
Plastic material	10
Gum-arabic sorts	0.2

The plastic part was a mix of alumina and uncalcined clay of the same average composition as the grog. The whole was wetted to a soft consistency and hand-tamped in a steel mold, dried, and burned in an oil-fired kiln.

The vitreous sillimanite proved almost worthless when made into brick. The brick were fired at temperatures exceeding 1,600° C. for periods as long as 48 hours, and were dense and hard when they came from the furnace. Without exception, they failed in the load test, under a pressure of 25 lb. per sq. in. (1.75 kg. per sq. cm.) at a temperature between 1,450° and 1,500° C. There was some slumping, but the failure was mainly due to shearing and splitting. A block of fused silica also failed at this temperature under the same unit pressure, while a block of vitreous sillimanite could not be crushed in the kiln. These tests, together with the fact that the cleavage was between the grog particles, leaving them sharp and unchanged, shows that failure of the brick was due to the matrix of glass surrounding all the

crystals of sillimanite. In the case of the sillimanite block, the glass had no effect because of the interlocking skeleton of crystals.

Brick made from the stony sillimanite, when insufficiently fired, also failed under load test; but when fired for about 48 hours at 1,600° C. or more, there was a re-growth of crystals that caused the particles of grog to lose their identity, and made a cross-section of the brick appear uniform and homogeneous. These brick stood up under the load test to 1,700° C. (the limit of the test kiln), without showing any noticeable deformation. These load-test results were better than those given by any commercial brick, with the exception of the re-crystallized silicon carbide brick sold under the name of refrax.

Laboratory tests have proved sillimanite brick to be more resistant to spalling than either silica or magnesite brick.

The Howe[13] cone-fusion slag test is carried out by finely grinding a refractory material and mixing it with definite amounts of finely-ground slag, after which the mixture is molded into cones. These cones are then fused beside Seger-Orton cones, and the lowering of the fusion point caused by the slag is noted. When tested under these conditions, sillimanite appeared to be more readily attacked by basic slags than magnesia, and affected more by acid slags than silica. This test, however, is not considered thoroughly reliable, because discrepancies have been found which throw doubt on its usefulness in foretelling the ability of a brick to withstand slag action.

A more representative test is that in which sillimanite brick and the brick with which it was compared were partly immersed in a bath of molten slag for a definite period of time and the effects noted. Here the relative inertness of sillimanite, and the dense interlocking-crystalline structure of the brick, showed to advantage. Tested in parallel with silica and magnesite brick in a high-lime slag, the sillimanite remained standing and lost approximately one-tenth of its weight, the silica brick completely disappeared, and the magnesite brick disintegrated into such small pieces that they could not be recovered. The sillimanite brick

[13] Howe, Raymond M., Refractories for electric furnaces: Book on "Refractories for Electric Furnaces," published by the American Electrochemical Society, 1924, pp. 3-17, incl.

showed no penetration of slag. In an oxidizing slag of high-iron content, the above results were practically duplicated. In an acid slag, the magnesite brick practically disappeared, whereas both the silica and sillimanite bricks presented merely a washed appearance, although the silica brick had spalled badly above the slag line.

Effect of Impurities.

While all impurities have the effect of lowering the melting point of refractories, lime seems to be the arch enemy of sillimanite. Iron can be reduced to the point where it does little harm, and magnesia is usually present only in small quantities. But lime is apt to be present in the raw materials, and when it exceeds 1.5 per cent in the sillimanite, it causes a serious drop in the fusion temperature. Table II shows clearly the deleterious effect of lime. It is apparent from the fusion of melt No. 74 that there is a limit to the bad effect of lime, but this lower limit is quickly reached. Alkalis would undoubtedly lower the melting point, but no data on them are at hand, although there is some reason to believe that alkalis are partly vaporized during melting.

TABLE II.

Analyses and Fusing Temperatures of Artificial Sillimanite Bricks.

Melt No.	SiO_2 Per cent	Al_2O_3 Per cent	FeO Per cent	CaO Per cent	MgO Per cent	Cone fusion	Approx. temp. ° C.
64	32.5	64	0.10	2.6	1.1	No. 27	1610
65	31.4	64	0.20	3.1	0.9	29	1650
68	29.2	68	0.28	1.5	0.7	38	1810
72	26.9	70	0.42	1.6	0.7	36	1770
73	27.0	69	0.28	3.4	0.4	±10	1350
74	27.3	66	0.70	5.0	0.7	±10	1350

SUMMARY.

Neither indirect nor direct-arc furnaces seem practical for the melting of aluminum silicate, because of the low-heat and elec-

trical conductivities of this substance. A furnace employing resistance heating, with the electrodes fairly close together and the current flowing through the molten bath, gave the best results.

Artificial sillimanite may be prepared by melting materials of the proper proportions of alumina and silica, or by melting clay and removing the excess silica by reduction with carbon. The silica is removed partly as Si and partly as SiO.

Although natural sillimanite has the composition $Al_2O_3.SiO_2$ with an alumina silica ratio of 63 : 37, artificial sillimanite always has the composition $3Al_2O_3.2SiO_2$ with a ratio of 72 : 28.

Artificial sillimanite of an alumina content below the 3 : 2 composition crystallizes in long vitreous needles, but that above this ratio is stony and finely-crystallized.

As a refractory, the vitreous material is inferior to the stony. The stony sillimanite brick, which may be called sillimanite-corundum brick, stand a higher load test than silica, spall less than either silica or magnesite, last longer than either silica or magnesite in a high-lime or high-iron slag, and are as good as silica in an acid slag.

When lime as an impurity in sillimanite exceeds 1.5 per cent., it causes a serious reduction in the fusing temperature.

Acknowledgment is given to Clyde E. Williams, superintendent of the Northwest Station, under whose direction this work was conducted.

DISCUSSION.

O. B. WESTMONT[14]: What is the consistency and workability of that wet mix? You will notice that there is 50 per cent of very coarse material put through 2 mesh on 4 mesh (8 and 16 meshes per 10 cm.) and 40 per cent of fairly fine material, but no intermediate grades, and I wonder just how that material worked up in the plastic state.

C. E. SIMS: The mix before firing did seem rather dry, but upon firing the bonding material, which consisted of a mixture of

[14] Research Chemist, Carborundum Co., Niagara Falls, N. Y.

a plastic clay and aluminum oxide in proportion to form $3Al_2O_3 . SiO_2$, caused a transformation, or rather, it transformed itself, into crystallized sillimanite. The final product, instead of being a mixture of a bond and grog, was a re-crystallized brick, and a section of that brick would show practically a homogeneous surface, and the particles of grog in the bond could not be detected. This change does not occur, however, when glass is present in the lower alumina compositions, glass seeming to prevent the conversion into sillimanite.

A paper presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 3, 1924, Mr. F. A. J. FitzGerald in the Chair.

FLUORINE IN THE DEOXIDIZING SLAG, AND ITS INFLUENCE ON REFRACTORIES IN BASIC ELECTRIC FURNACE PRACTICE.[1]

By Frank T. Sisco.[2]

Abstract.

The deoxidizing slag in basic electric furnace practice is made up of lime, coke, and fluorspar in the ratio of approximately 6:1:1. At the high temperature present in the deoxidation period, the fluorspar is acted upon by oxygen, oxides, carbon, or by heat alone. The fluorine set free reacts with silica in the roof and upper walls to form silicon tetrafluoride. Part of this constituent probably escapes; another part drips into the slag where it reacts with lime to form calcium silico-fluoride. These reactions are going on continuously during the deoxidation period, and are dependent upon the temperature and the amount of fluorspar used. The activity of fluorine results in an increase in the silica content of the slag at the expense of the roof and side walls. This enrichment amounts to 100 lb. of silica or more each heat, and results in one-quarter to one-half of the total weight of the roof and upper side walls being worn away during the life of the refractories.

Fluidity, a most desirable and essential characteristic of the deoxidizing slag is obtained, when fluorspar is used, by the formation of calcium silicates and calcium silico-fluorides, and by the presence of calcium fluoride. When silica sand is substituted, wholly or in part, for fluorspar the fluidity is obtained mostly by the formation of calcium silicate. With fluorspar, it is possible to maintain a much higher degree of basicity for the same fluidity than is possible with silica sand. This is one advantage of the use of fluorspar. Another advantage is that fluorspar is a direct aid in desulfurizing, while silica sand is not. The third and most im-

[1] Manuscript received July 1, 1924.

[2] Metallurgist, Air Service, War Department, McCook Field, Dayton, Ohio.

portant advantage is that it is much easier to maintain strongly reducing conditions, by an excess of calcium carbide, if fluorspar is used. These reducing conditions are necessary to the production of sound, clean steel.

By the proper use of fluorspar, the corrosion of the refractories, while considerable, is not dangerous, and does not shorten refractory life sufficiently to warrant discontinuing the use of this thinning agent.

The use of too much fluorspar, or a too high temperature, or both, causes the slag to become thin and watery. In this condition it is smooth and mirror-like and reflects a greater part of the heat from the arcs to the roof and upper side walls, causing them to become overheated and drip. In addition to the reduced life of the refractories, this condition results in a rapid change in the slag composition, destroying reducing constituents, such as calcium carbide, almost immediately.

Refractory life may be shortened by the action of lime dust on the exposed surface of the hot acid brick. Calcium silicate is the result of this action. This constituent melts easily, and thus exposes a fresh surface of the brick to attack. This untoward condition may be almost wholly prevented, or largely minimized at least, by intelligent furnace operation.

INTRODUCTION.

It has been often observed by operators of basic electric furnaces that the composition and condition of the deoxidizing slag has some influence upon the condition and life of the furnace refractories, and, conversely, it is well recognized that the condition of the furnace refractories may have a vital influence upon the composition and condition of the slag. These two factors are closely related and, consequently, cannot be discussed apart from each other.

A few years ago the writer had the opportunity of observing, for several months, the furnace practice with a 30-ton basic lined Heroult, at a government steel plant in the East. Some of the difficulties encountered with the deoxidizing slag at that plant led to the opinion that fluorspar was far more active in the deoxidizing slag than was commonly supposed. This supposition was

upheld further by experience with deoxidizing slags on 6-ton Heroult furnaces melting cold scrap, in that as soon as silica sand was substituted for fluorspar in the slag, some of the old difficulties were eliminated, but others arose in their places.

Work done at the government plant in the chemical analysis of these slags demonstrated beyond doubt that not only fluorides, but also silico-fluorides, were constituents. Further work at a later date proved the supposition, long held by some furnace melters, that the composition and condition of the slag and the condition of the refractories were so closely related that it may be said that refractory life depends to a large extent upon the slag composition and condition, and that the condition and composition of the slag and of the metal as well depends upon the influence that the refractories may have on the slag.

THE REFRACTORIES.

The refractories used in basic electric furnace practice may be divided into three groups according to their location in the melting chamber. These are: (1) The bottom and banks of magnesite; (2) the side walls of silica, and (3) the roof of silica.

The bottom and banks of magnesite may be constructed in any one of the numerous ways accepted as standard practice. In general, the side walls of silica brick are laid with headers exposed and may or may not be separated from the magnesite by one or two courses of chrome brick. The roof is constructed of either special or standard shapes. The advantages and disadvantages of each kind of brick are well known and need no further comment.

It may be said here that slag condition and composition probably have more influence on the upper walls and the roof than on any other section of the furnace refractories, and are a great factor in either preserving or shortening the life of this part of the lining.

THE DEOXIDIZING SLAG AS FIRST FORMED.

After oxidation is completed and the oxidizing slag removed in the cold scrap process, or after the duplexed open-hearth metal is poured into the electric furnace in the hot metal process, the deoxidizing slag is put on the metal. The slag is made up of 5 to

10 parts of lime, 1 to 3 parts of powdered coke, and 1 to 3 parts of fluorspar. These materials may be mixed on the furnace floor before shoveling into the furnace, or may be added to the furnace separately.

As soon as the slag has been thrown into the furnace, part of the coke burns to carbon monoxide, filling the furnace with a reducing gas. Another part of the coke reacts with metallic oxides floating on the metal (ferrous and manganous oxides, FeO and MnO), and with the metallic oxides in the slag-making materials, reducing them to their respective metals. As this deoxidation of the slag proceeds, the color of the slag changes from brown or greenish brown to light brown and finally to white; the latter denoting that deoxidation of the slag is practically complete. These colors represent the appearance of a spoonful of the slag cooled in air.

To accomplish a complete deoxidation, and a complete desulfurization as well, it is necessary that an appreciable amount of calcium carbide be present constantly. To maintain the required amount the slag should be very basic, sufficiently fluid, but not too much so, and contain an excess of carbon. To this end the furnaceman makes additions of lime, coke and fluorspar either together or separately at intervals during the final period.

Most operators of basic electric furnaces have considered that fluorspar was not contained permanently as such in the deoxidizing slag. It was assumed that the fluorine would be expelled and pass off as a gas soon after the fluorspar was added. Probably no one has investigated the role of this element under the influence of the arc. So long as the furnaceman obtained the slag fluidity he desired, he worried little about the cause of this fluidity. For several years the writer had noticed that a complete chemical analysis of electric furnace deoxidizing slags would seldom total to 100 per cent, but under the pressure of wartime operation had no opportunity to ascertain the cause.

The investigation of the action of fluorine in the deoxidizing slag had its inception when a sample of slag from a 30-ton basic lined Heroult furnace was analyzed by standard methods and found to contain only a trace of silica. Knowing that the lime used for the slag contained a considerable percentage and that an appreciable amount was present in both the coke ash and the

fluorspar, it was decided to discover, if possible, what had become of the silica that should normally be present. The history of the heat was investigated and it was found that 40 min. before the sample was taken the slag had been thick and viscous, due to a large patch of the bottom coming up. More than 100 lb. (45.4 kg.) of fluorspar were necessary to thin the slag. As soon as the slag had thinned the sample was taken.

FLUORIDES AND SILICO-FLUORIDES IN THE SLAG.

When it was found that the apparent absence of silica could be traced to the fluorspar addition, it was surmised that various compounds of lime, fluorine and silica were probably formed and were present in the slag. To prove this it was necessary to work out a new method for the chemical analysis[3] of these compounds.

Using the new method for analysis, it was shown that electric furnace deoxidizing slags were complex mixtures of silicates, fluorides, and silico-fluorides. Some representative analyses of deoxidizing slags are given in Table I.

Sample No. 1 shows typically how much fluorine may be present in the slag. The fluorine as calcium fluoride is 28.40 per cent. All of the fluorine is not present as calcium fluoride, CaF_2; a considerable quantity is present as a compound of calcium, silicon and fluorine, probably as calcium silico-fluoride, $CaSiF_6$. The difference between the true silica, 9.65 per cent, and the total silica, 13.17 per cent, represents the silica probably existing as a silico-fluoride.

Part of the fluorine present in the slag in sample No. 1 has been lost by volatilization one hour later, as sample No. 2 has only 10.45 per cent fluorine as calcium fluoride present. This decrease was not wholly caused by volatilization, but was due, to a slight extent, to an increase in slag volume from various additions of lime and coke during the hour that elapsed between samples 1 and 2. The amount of silico-fluoride has also decreased appreciably, as the difference between the total silica and true silica, or 3.52 per cent in sample No. 1, has dropped to 1.55 per cent in sample No. 2. This decrease was due almost wholly to the volatilization of the fluorine, or to a chemical reaction between silicates and silico-fluorides in the slag.

[3] See addendum, page 543.

TABLE I.

Analyses of Electric Furnace Deoxidizing Slags.

(In per cent by weight)

Constituent	Slag No. 1		Slag No. 2		Slag No. 3		Slag No. 4
	Proximate	Complete	Proximate	Complete	Proximate	Complete	Complete
Silica, SiO_2, true.....	9.65	*	16.35	*	17.45	*	26.09
Silica, SiO_2, total.....	*	13.17	*	17.90	*	18.25	*
Iron oxide, FeO.....	1.08	1.08	0.41	0.41	1.01	1.01	2.43
Manganese oxide, MnO.	0.13	0.13	0.08	0.08	0.47	0.47	0.64
Aluminum oxide, Al_2O_3..	3.17	3.17	3.52	3.52	4.63	4.63	2.17
Calcium as oxide, CaO..	64.85	40.29	60.37	52.71	60.13	57.61	54.81
Calcium as fluoride, CaF_2	*	28.40	*	10.45	*	5.67	none
Magnesium oxide, MgO.	11.13	11.13	10.17	10.17	10.75	10.75	12.41
Calcium sulfide, CaS....	2.07	2.07	2.61	2.61	1.24	1.24	1.01
Calcium carbide, CaC_2...	none	none	1.25	1.25	none	none	none
Free carbon, C.....	0.43	0.42	0.52	0.52	trace	trace	0.17
Total	92.51	99.87	95.28	99.62	95.68	99.63	99.73

* Undetermined.

Analyses from writer's private notes.

Slag No. 1. From 6-ton basic lined Heroult. After adding 100 lb. (45.4 kg.) of fluorspar. Slag thin and watery.

Slag No. 2. Same slag as No. 1, one hour later. Slag fluffy and in good condition.

Slag No. 3. From 6-ton basic lined Heroult. Slag made with some fluorspar and some silica sand. Slag thick.

Slag No. 4. From 6-ton basic lined Heroult. Slag made with sand; no fluorspar used.

The decrease in the amount of fluorine present was accompanied by a decided change in the physical condition of the slag. When sample No. 1 was taken the slag was thin and watery. One hour later it was fluffy, foamy and in good shape.

Slag No. 3 was made according to standard practice, except that part of the fluorspar was replaced by silica sand. The slag was pure white in color and in fairly good condition. The ferrous and manganese oxide contents are somewhat above normal; the former should be below 0.50 per cent and the latter little more than a trace. In this sample there is only a small amount of fluorine, as indicated by the amount (5.67 per cent) of calcium fluoride, and only a small amount of silica (0.80 per cent) is present as a silico-fluoride.

Slag No. 4 is a typical deoxidizing slag made with silica sand. In this case no fluorine is present at all, consequently the true silica is also the total silica, as none could be present as silicofluoride.

ADVANTAGES AND DISADVANTAGES OF FLUORINE IN THE DEOXIDIZING SLAG.

It is generally admitted by furnacemen that a deoxidizing slag, made by substituting silica sand wholly or in part for fluorspar, is much more difficult to keep strongly reducing in its action. Just why this is so, the writer is not prepared to say, but from his own experience, and from the word of others, it is comparatively difficult to form calcium carbide, and exceedingly difficult to keep it in the slag in appreciable amounts, unless fluorspar is used almost wholly as a thinning agent.

In addition to the value of fluorspar in promoting carbide formation, it also aids in desulfurization. Experience has shown that desulfurization is never so certain, nor so complete when silica sand is used in the slag. Fluorspar is a desulfurizing agent in itself, and in addition promotes sulfur elimination by conferring fluidity and assisting in keeping the slag sufficiently basic and reducing in its action. The fluidity obtained by fluorine is not with so great a sacrifice of basicity, as is the case when silica sand is used. In view of these facts, we can safely state that fluorine is an exceedingly valuable aid in deoxidizing and desulfurizing, and that its substitution, wholly or in part, by silica sand results in decreased slag efficiency. We shall have occasion to refer to this again.

The one disadvantage in the use of fluorspar is the corrosive action of fluorine or fluorides on the furnace roof and walls.

Corrosion of the Roof and Walls by Fluorine and Its Effect Upon the Silica Content of the Slag.

To illustrate the corrosion of the roof and side walls, we will take the slag analysis made on an experimental heat in a 6-ton basic lined Heroult furnace. In general, the results recorded in Table II are self-explanatory. The method of making slag additions to the heat, shown in Table II, is by no means representative

TABLE II.

Changes in Slag Composition During the Deoxidation Period.

Time	Additions to Slag, lb. (100 lb. = 45.4 kg.)	SiO_2 True Per Cent	SiO_2 Total Per Cent	FeO Per Cent	MnO Per Cent	Al_2O_3 Per Cent	CaO Per Cent	CaF_2 Per Cent	MgO Per Cent	CaS Per Cent	CaC_2 Per Cent	Free Carbon Per Cent	Appearance of Slag
11.05	Lime, 600 Fluorspar, 100												
11.30	Sample taken.	4.53	6.05	4.31	1.25	2.65	61.47	13.62	10.13	0.23	nil	nil	Light greenish - brown. Thick, viscous, cold.
11.35	Coke, 65 Fluorspar, 60												
12.00	Sample taken.	5.20	9.78	1.55	0.63	2.51	49.72	23.48	10.37	1.06	nil	0.30	Very light brown. Thin watery, warmer.
12.05	Coke, 50												
12.30	Sample taken.	10.12	16.91	0.60	0.13	2.94	48.51	18.40	9.75	1.44	0.45	0.68	Grayish - white. Thin, getting hot.
12.55	Lime, 150												
1.00	Sample taken.	15.25	17.08	0.85	0.12	3.01	54.71	11.83	9.81	1.93	trace	0.31	White. Fluffy and hot. Condition good. No carbide.
1.05	Coke, 50 Fluorspar, 35												
1.30	Sample taken.	16.35	18.27	0.41	trace	2.96	50.17	15.13	9.45	2.27	0.88	0.57	Grayish-white. Carbide. Fluffy and hot. Condition excellent.
1.35	No addition made												
2.00	Sample taken.	16.83	18.31	0.27	0.06	3.06	55.16	10.17	10.21	2.37	0.27	0.31	Almost white. Slightly carbide. Hot. Condition good.
2.05	Lime, 50 Coke, 30 Fluorspar, 20												
2.30	Sample taken.	17.68	18.90	0.31	trace	2.90	51.47	11.58	10.58	2.85	1.08	0.47	Dark gray. Strongly carbide. Hot. Condition excellent.
2.35	No addition made												
3.00	Sample just before tap.....	18.31	19.17	0.25	trace	3.28	56.17	6.32	10.81	2.88	0.65	0.31	Gray. Carbide. Condition excellent.

of good furnace practice, as the slag-making materials were added in the manner indicated to investigate the specific effect of fluorine or fluorides. In regular practice nearly all of the slag is added at once, and only a small amount of lime, coke, and spar added during the rest of the heat to keep the slag in good condition.

It will be noted from Table III that the percentage of silica in the lime and fluorspar is less than 5. In the coke probably less than 5 per cent is silica. Twenty-five minutes after the addition of 600 pounds of lime and 100 pounds of fluorspar there is 6.05 per cent silica present in the slag. Thirty minutes later 9.78 per cent is present, and at 12.30, one hour later, 16.91 per cent is present.

TABLE III.

Analysis of Lime and Fluorspar Used in the Slag of Table II.

	Lime Per Cent	Fluorspar Per Cent
Silica	5.47	2.91
Aluminum and iron oxide	1.20	0.65
Calcium oxide	83.34	.....
Magnesium oxide	8.63	.....
Calcium fluoride	.....	90.51
Calcium carbonate	.....	5.48

The percentage of silica increases progressively from 6.05 per cent to 19.17 per cent. Assuming that the slag-making materials contained 5 per cent silica and that the total slag weighed 1,200 lb. the silica enrichment during the deoxidation period was 140 lb., of which the greater part came from the roof and walls. In the daily practice this is probably close to 100 lb. or 10,000 to 15,000 lb. for a lining and roof of average life, in a 6-ton basic furnace. These figures show that from one-quarter to one-half or more of the lining and roof goes into the slag during their life of 100 to 150 heats.

It should be noted, however, that the corrosion of the roof and upper walls by fluorine or fluoride is likely to be uniformly distributed, consequently it is not usually the direct cause of failure, although when the lining and roof become relatively thin, failure caused by uneven expansion and contraction may be hastened.

SILICA SAND AND FLUIDITY.

The use of silica sand to replace fluorspar, either wholly or in part, has gained in favor because furnacemen have realized that fluorine had some ill effect on the refractories. Using sand, the fluidity necessary could be obtained by the formation of calcium silicates. It has been frequently argued that when fluospar is used, the deoxidizing slag adjusts itself to about 20 per cent silica anyway, so why not add that amount of silica at the start and eliminate fluorspar? This, however, is only partly true. In the slag made with fluorspar the silica will increase steadily, but it will not adjust itself to any definite ratio of acids to bases. The silica in the average slag made with spar will be much nearer 16 to 18 per cent than to 20 per cent. When sand is used, ordinarily the silica will be more than 20 per cent before the desired fluidity is attained.

One of the chief factors in obtaining fluidity is by the formation of calcium silico-fluoride. This constituent when associated with calcium fluoride and calcium silicate makes the slag much more fluid with the same percentage of acids (silica) than when calcium silicate alone is present. Thus the slag may be kept relatively much more basic, and thus more efficient, and still have the necessary fluidity.

The corrosion of the roof and side walls by fluorine is a serious matter, but it is not so serious as an imperfectly deoxidized steel, and there is no question but that the slag is much more efficient in deoxidizing if fluorspar is used as a thinning agent. And in addition, as fluorspar is a direct aid in desulfurizing, while silica sand is not, this alone would make the use of fluorspar justified even at the sacrifice of a few heats on the walls and roof.

It is true that when excessive amounts of fluorspar are used the percentage of silica in the slag increases rapidly at the expense of the roof and walls. In good furnace practice, the slag is never permitted to get so thin and watery that fluorine corrosion becomes excessive. The proper carbide slag will contain about 10 per cent fluorine as calcium fluoride, and 1 to 3 per cent silica as silico-fluoride.

TEMPERATURE AND FLUIDITY OF SLAG AND THEIR EFFECT ON THE ROOF AND WALLS.

There are other factors in the condition of the deoxidizing slag that affect the condition and thus the life of the refractories. These untoward conditions in the slag, causing untoward conditions in the roof and walls, are reflected back to the slag composition, and thus affect the deoxidation of the molten bath.

The principal factor in causing a bad slag condition is overheating the roof and walls. Another factor, but with more influence on the lining and roof than on the slag, is the formation of calcium silicate by the reaction between the silica brick and lime dust. A third factor which might be discussed incidentally is the influence on the slag of patches of the bottom coming up.

Overheating the Roof and Walls.

An excessively thin, watery slag, due to the use of too much fluorspar, a too high temperature, or both, nearly always causes overheating of the roof and to some extent of the upper side walls. The thin, watery slag is smooth and mirror-like and lies quietly, thus producing a maximum amount of reflection. The heat from the arcs is, to a large measure, reflected upward and affects the roof brick, quickly causing them to drip. As the liquid silica drips into the slag, the amount of silica increases rapidly, any carbide present is destroyed or prevented from being formed, and the process of furnace deoxidation is stopped almost at once.

It is quite surprising how quickly a dripping roof will affect the composition of the slag. In one instance the combined ferrous and manganese oxide content in the slag increased from 0.61 per cent to 4.74 per cent in 12 min.[4] An increase in the oxide content in the metal bath would be the result of this increase in oxides in the slag. It is evident that overheating the roof may be almost prevented by intelligent furnace operation.

The use of too much fluorspar is, therefore, accompanied by two evils, so far as the roof and walls are concerned: (1) The thin, watery slag resulting from an overdose of spar produces a maximum amount of heat reflection, and may cause the roof

[4] Cited in Sisco; "The Manufacture of Electric Steel"; McGraw-Hill Book Co., p. 165 (1924).

or upper walls to drip, and (2) the large amount of fluorine present in the slag promotes the rapid corrosion of the silica refractories. Both of these evils result in an unsatisfactory slag condition; the silica content increases too fast and deoxidation may be retarded or even stopped altogether.

The Reaction Between the Silica Brick and Lime Dust.

In shoveling lime into the furnace the melting chamber becomes filled with a fine, powdery dust, which may react with the hot exposed surface of the silica brick in walls and roof to form calcium silicate. If the refractories are sufficiently hot, this calcium silicate will melt as fast as formed and will drip into the slag, thus exposing a fresh surface of the brick to attack.

Wearing away the brick by the formation of calcium silicate is not especially serious, as in good furnace practice only two, seldom more than three, additions of lime are necessary in the deoxidation period. It does, however, become serious when the furnaceman, as is the habit with many, adds a shovelful or two every few minutes.

Influence of the Bottom Coming Up on the Deoxidizing Slag.

There is usually little trouble with the bottom in the deoxidation period. Unless the heat is in the furnace an unusually long time, only a small amount of the dolomitic refractory works loose and comes up to contaminate the slag. Some bottom trouble may be encountered in melting and oxidizing in the cold scrap process. Any refractory working loose then will be carried away by the oxidizing slag. The absence of bottom trouble, of course, predicates an excellent bottom to start with, one firmly sintered and free from cracks, into which the metal may seep during the final refining. In good furnace practice we may say that metal and slag will have practically no effect upon the refractories in the bottom.

Should a patch of the bottom work loose during the deoxidizing period, its effect upon the slag composition and condition can be noticed almost immediately. The high magnesia refractory makes the slag thick and viscous. The iron oxide in the dolomite or magnesite, which may amount to 6 or 8 per cent, reacts with any

calcium carbide in the slag and tends to destroy the existing reducing conditions. When any of the bottom comes up it is necessary to add excess of fluorspar, and follow this with powdered coke to bring the slag into shape again.

ADDENDUM. NOTE ON THE CHEMICAL ANALYSIS OF ELECTRIC FURNACE DEOXIDIZING SLAGS.

True Silica. In the standard method for slag analysis, a 0.5 g. sample is dissolved in hydrochloric acid or fused with sodium carbonate. If a fusion is made it is extracted with water and acidified with hydrochloric acid. The acid solution is evaporated to dryness and baked to dehydrate the silica. The dry salts are dissolved in dilute hydrochloric acid and the solution filtered. The silica is washed thoroughly and after drying is ignited and weighed. This method gives the silica existing as silicate and is designated true silica. Any silica present as a silico-fluoride will form silicon tetrafluoride on the addition of hydrochloric acid to the slag, or to an alkali fusion of the slag, and will pass off as a gas. Consequently, the silica existing as a silico-fluoride cannot be determined by the usual methods.

The presence of much silico-fluoride in a slag may be detected by placing a little slag in a beaker, adding concentrated hydrochloric acid, and covering with a watch glass. The silica evolved as silicon tetrafluoride will etch the cover glass.

Total Silica. For total silica, 20 cc. of concentrated acetic acid are added to 0.5 g. of the slag contained in a small beaker. After digesting at a temperature slightly below the boiling point for an hour, the solution is diluted, heated, filtered and washed. The paper and residue is ignited to constant weight at a low temperature and cooled and weighed.

After weighing, the silica is volatilized by the addition of 5 cc. of hydrofluoric acid and the application of gentle heat. The crucible and contents are ignited, cooled, and weighed as before. A second volatilization is usually necessary to expel all of the silica. The loss in weight is total silica.

This result includes the silica existing in the slag as silicate and as silico-fluoride. By subtracting the percentage of true silica

from the total silica, the silica present as silico-fluoride can be determined.

Other Elements. Other elements are determined by standard methods.[5] No difficulty is experienced with the possible exception of the determination of fluorine as calcium fluoride.

When electric furnace deoxidizing slags are analyzed by standard methods, two errors are introduced. The first consists of determining only the silica existing as silicate. The second is in calculating all of the calcium determined, to the oxide (and sulfide), whereas it exists as the oxide (silicate), the fluoride or silico-fluoride.

ACKNOWLEDGMENT.

The writer wishes to acknowledge his indebtedness to Harry Schagrin, chief chemist at the U. S. Naval Ordnance Plant, Charleston, W. Va. (1921), under whose supervision the methods of chemical analysis for deoxidizing slags were worked out; and who contributed many valuable suggestions on the action of fluorine in the deoxidation period in basic electric furnace practice.

DISCUSSION.

W. C. Moore[6]: It seems to me that a plausible explanation of the action, whereby the roof of Mr. Sisco's furnace is attacked, can be given. For a number of years I made up a mixture of silica and calcium fluoride. When these materials were mixed at about 900° C. the calcium fluoride commenced to react, and the only definite explanation which I can give for the tendency to react is that at that temperature calcium fluoride begins to volatilize somewhat. So that the better explanation of the increment of silica in Mr. Sisco's slag would be the volatility of calcium fluoride, which would react then with the silica of the roof to form calcium silicate and calcium fluosilicate.

C. E. Williams[7]: The attacking of silica roofs and side walls by fluorspar can, I believe, be explained by the single reaction:

[5] See Sisco, "Technical Analysis of Steel and Steel Works Materials," McGraw-Hill Book Co., pp. 491-502 (1923).

[6] Research Chemist, U. S. Industrial Alcohol Co., Baltimore, Md.

[7] Supt., Northwest Exp. Station, U. S. Bureau of Mines, Seattle, Wash.

$$2CaF_2 + 3SiO_2 = 2CaSiO_3 + SiF_4.$$

Silicon tetrafluoride, being a gas, would escape and thus assist the reaction to take place as indicated. Calcium fluosilicate ($CaSiF_6$) may be formed as indicated by Mr. Sisco, but would probably decompose giving the final products I have indicated above. That is:

$$\begin{array}{l} 3CaF_2 + 3SiO_2 = CaSiF_6 + 2CaSiO_3 \\ CaSiF_6 = CaF_2 + SiF_4 \\ \hline 2CaF_2 + 3SiO_2 = 2CaSiO_3 + SiF_4. \end{array}$$

I do not know whether the boiling point of CaF_2 has been determined, but it is known that many halide salts have fairly low boiling points and that they exert relatively high vapor pressures at temperatures below their boiling points. It is reasonable to assume that CaF_2 is vaporized at the temperature of the steel furnace slag, and that CaF_2 would vaporize before decomposing into its elements. It seems logical, therefore, to expect that calcium fluoride vaporizes and reacts with the silica of the roof and side walls, forming gaseous silicon tetrafluoride, which escapes, and calcium silicate which runs down into the slag. I found that fumes from a furnace containing a large quantity of fluorspar-silica slag gave an acid reaction when dissolved in water, due, no doubt, to the formation of hydrofluosilicic acid:

$$3SiF_4 + 2H_2O = 2H_2SiF_6 + SiO_2.$$

Mr. Sisco's method of determining "true silica" (p. 543) will not yield all the silica in a sample containing CaF_2, because the treatment with hydrochloric acid would cause some loss of silica by the formation of hydrofluoric acid, which would convert silica to the volatile SiF_4.

D. H. Killeffer[8] (*Communicated*): The presence of silicofluorides in the final melt may be easily accounted for by the reaction:

$$3CaF_2 + SiO_2 = 2CaO + CaSiF_6.$$

This reaction involves no such improbability as free fluorine. Nor is it impossible in this way to account for the reduced fluorine

[8] Assoc. Editor, Ind. and Eng. Chemistry, New York City.

content of the final slag, which may well occur through the thermal decomposition of the calcium silicofluoride to form silicon tetrafluoride and the original fluorspar.

L. KAHLENBERG[9] (*Communicated*): Fluorine is an extremely active element, and considering the ingredients of the slag, there are plenty of substances present to bind fluorine chemically.

The presence of silico fluorides in the slag due to the use of fluorspar could be accounted for by the equation:

$$3CaF_2 + 3SiO_2 = CaSiF_6 + 2CaSiO_3.$$

JOEL H. HILDEBRAND[10] (*Communicated*): Although there are no measurements of the free energy of fluorine compounds, their chemical behavior indicates that at least at moderate temperature they are much more stable than the corresponding oxygen compounds. The main reaction causing the escape of fluorine should, I believe, be regarded as

$$2CaF_2 + SiO_2 = 2CaO + SiF_4.$$

This reaction would naturally occur easily on account of the volatility of the SiF_4. It can be readily seen that the presence of SiO_2 in excess would use up the CaO necessary to keep the slag basic.

Of course, we have little direct evidence for the reactions occurring in such a furnace at arc temperature, but the corrosion of the roof can, I think, be plausibly explained by assuming sufficient volatility of CaF_2 at arc temperatures to bring about the above reaction upon the roof of the furnace.[11]

F. J. HAMBLY[12] (*Communicated*): There is undoubtedly a great deal of purely chemical work yet to be done regarding the behavior of fluorine compounds at temperatures even approaching those existent in a steel furnace. Instead of assuming the existence of free fluorine in the gases of the furnace chamber, it would appear to be more feasible to attribute the increased corrosion of the silica roof and side walls of the furnace to volatilized metallic fluorides (possibly iron) acting upon the heated

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[11] J. Am. Chem. Soc., 46, 2175, 2179, 2183, 2223 (1924).
[12] Mgr., Electric Reduction Co., Ltd., Buckingham, Que., Canada.

silica of the roof, forming silicon fluoride and readily fusible silicates (or fluo-silicates), which would account for the increased wear of the roof, in excess of that caused by the lime dust when no fluorspar is used.

With the gradually increasing percentage of silica in the slag, the loss of fluorine is readily accounted for by the well-known formation of gaseous silicon fluoride from interaction between calcium fluoride and silica. The statement on p. 540 that "the use of silica sand to replace fluorspar, either wholly or in part, has gained in favor" would appear to agree with the foregoing suggestions, as when a mixture of fluorspar and silica sand is used in the furnace, silicon fluoride would probably be the principal fluorine compound in the gases, and would not attack the silica roof in the way that any other volatile fluorine compound might be expected to do.

In the analyses of slags given in the paper, a distinction is made between "true" silica and silica present as silico-fluorides, but calcium fluoride is the only fluorine compound shown in Tables I and II. Is it to be understood that the *total* fluorine in the slags has been calculated as calcium fluoride, or, that fluorine present as silicofluorides has not been included in the analyses? A note should be added to the tables to elucidate this point and to explain how the oxygen equivalent for the fluorine as silico-fluoride has been taken care of.

While not directly connected with the subject of electric furnace practice, it is perhaps of interest to recall here that Bainbridge[13] obtained and identified from a basic open-hearth slag, to which fluorspar had been added, crystals of apatite

$$3(3CaO.\ P_2O_5)\ CaF_2.$$

STEPHAN KRIZ[14]: The paper by Mr. Sisco is a very valuable contribution to the study of the deoxidizing slags in electric furnaces. The many unsolved problems in this field can only be cleared up by an experimental investigation. For example, we know very little of the stability of calcium carbide in slags containing calcium fluoride or silica, the different behavior of these two slags during deoxidization, etc. The publications to date

[13] Chem. Abstracts, **21**, 2687 (1921).

[14] Manager, Steel Works, Boetler Works, Düsseldorf, Germany.

dealing with the behavior of fluorides in the molten condition do not in any case suggest the production of free fluorine gas. In Mr. Sisco's case we wish to account for the excess of 160 pounds (73 kg.) of silica in the slag and how approximately a hundred pounds (45 kg.) of fluorine has escaped from the slag. Is it not possible that the introduction of silica into the slag may be due to a reaction between the fine lime dust passing through the arc and attacking the silica roof, producing low melting calcium silicates; and that the loss of fluorine in the slag may be due to a gradual interaction between the calcium fluoride and the silica according to the reaction:

$$2CaF_2 + SiO_2 = 2CaO + SiF_4?$$

I do not believe that Mr. Sisco's observed difference between true silicic acid and total silicic acid is to be ascribed to the presence of calcium silico fluorides, but is more readily explained by the action of the hydrochloric acid on the samples, giving rise to free hydrofluoric acid, which in turn acts upon the silica producing SiF_4.

If all metallurgists interested in electric furnaces would carry out experiments with the same enthusiasm and understanding as Mr. Sisco has done, we shall no doubt soon find a solution of the difficult slag problems.

Frank T. Sisco (*Communicated*): There is probably no practical method of proving definitely whether or not free fluorine exists in the furnace gases or whether silicon tetrafluoride, in some phase, is formed even momentarily.

In Table II the slag contained 9.78 per cent silica at 12 o'clock. Thirty minutes later it contained 16.91 per cent. This increase, assuming that the slag weighs about 1,000 pounds (454 kg.) is equivalent to 71.3 pounds (32.3 kg.) of silica. It is out of the question, for anyone familiar with furnace practice, to assume that this amount of silica could be eroded from the refractories in a 30-minute period, unless the furnace practice was very bad, or unless the erosion was due to some other cause than overheating or splashing of slag. In fact, in the particular heat summarized in Table II, extraordinary precautions were taken to prevent any untoward furnace conditions which might affect the refrac-

tories. In no case during this heat did the roof and upper side walls drip.

Mr. Killeffer explains silico-fluoride in the slag by the reaction of three molecules of calcium fluoride and one of silica to form two molecules of calcium oxide and one of calcium silico-fluoride. This reaction does not take into consideration the great stability of the various calcium silicates at furnace temperatures and the fact that in the slag there is little likelihood of any free silica being present. Of course, it is entirely possible that the reaction takes place; we can not say with certainty what does or does not happen at arc temperatures. The best we can do is to observe the results and guess at the cause.

The indisputable fact is that roof and upper side walls in 6-ton furnaces lose between 100 and 150 pounds (45.4 and 68 kg.) of silica per heat. In standard furnace practice it is out of the question that this amount is melted off from overheating, or from the formation of low-melting silicates on the surface of the refractories.

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